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November 23, 2010

Mr. Tien Q. Duong
EE-2G/Forrestal Building
Office of Vehicle Technologies
U.S. Department of Energy
1000 Independence Ave., S.W.
Washington D.C. 20585

Dear Tien,

Here is the fourth-quarter FY 2010 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://berc.lbl.gov/batt/.

Sincerely,

Venkat Srinivasan
Manager
BATT Program

edited by: V. Battaglia
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FEATURED HIGHLIGHTS

Cell Analysis and Cathodes –

- **Richardson and Doeff Groups develop a low-cost synthesis process for high-rate $LiFePO_4$.**
- **Zaghib Group develops an *in situ* SEM tool to directly observe the expansion/contraction of silicon oxide anodes during charge and discharge. With this tool they show that cracks formed during expansion, remain after contraction.**

Electrolytes –

- **Smith and Borodin Group confirm, through molecular dynamics simulations, the formation of dilithium ethylene dicarbonate in the SEI and not dilithium butylene dicarbonate.**

Cathodes –

- **Thackeray Group able to reduce first-cycle irreversible-capacity-loss and improve rate capability of a Li_2MnO_3-stabilized oxide with an acid treatment process.**

Diagnostics –

- **Kostecki Group measures different reactions and rates of electrolyte reduction on different crystalline surfaces of Sn.**

Modeling –

- **Newman Group accurately models the reduction current of a shuttle through an SEI.**

BATT TASK 1
CELL ANALYSIS

TASK STATUS REPORT

TASK 1.1 - PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Cell Fabrication and Materials Characterization

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: High energy system: low energy, poor cycle life

OBJECTIVES: 1) Bring fundamental understanding to electrode and cell construction. 2) Provide a comprehensive, independent assessment of promising materials with regard to meeting high-power or high-energy performance and cycling requirements, and differentiate between material and cell failure.

GENERAL APPROACH: Objective 1) is achieved through engineering design analysis of each of the steps of the electrode fabrication process and determining why certain configurations of binder and conductive additive work better for a given active material. Objective 2) is achieved through the identification and application of key diagnostic techniques that allow for the physical, chemical, thermal, and electrochemical characterization of materials as they relate to battery performance for advanced transportation applications.

STATUS OCT. 1, 2009: Correlations between electrode cyclability and mechanical strength are being developed. A new binder was synthesized for using Si nanoparticles as an anode: electrodes cycled at C/10 have shown a capacity of 2000 mAh/g for 150 cycles with little to no power fade after 40 cycles. A graphite has been selected as the new baseline, replacing MCMB. A new, high-voltage electrolyte showed improved coulombic efficiency when cycled in Li/NCM cells using cut-off voltages from 4.1 to 4.5 V. It was determined that VC has no measurable effect on the coulombic cycling efficiency of a graphite electrode.

EXPECTED STATUS SEP. 30, 2010: Correlation of electrode mechanical properties to cyclability will be established. The source of self discharge will be identified. We will know the extent to which the oxidation of the electrolyte is cathode material dependent. We will know the fundamental advantages and disadvantages of SBR binder.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:
(a) Report the coulombic efficiency of baseline NCM *vs.* graphite and *vs.* a lithium counterelectrode. (Jan. 10) **Complete**
(b) Report performance characteristics of a SBR-CMC-binder based anode. (Mar. 10) **Complete**
(c) Distribute electrodes cycled to different cut-off voltages to other members of the BATT program. (Apr. 10) **Complete**
(d) Report the results of the mechanical properties *vs.* cycling capability of NCM-PVdF-based cells. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

(a) Report the coulombic efficiency of baseline NCM *vs.* graphite and *vs.* a lithium counterelectrode. (Jan. 10) **Complete**. See 2nd Quarter Report.

(b) Report performance characteristics of a SBR-CMC-binder based anode. (Mar. 10) **Complete**. See 1st Quarter Report.

(c) Distribute electrodes cycled to different cut-off voltages to other members of the BATT program. (Apr. 10) **Complete**. See 3rd Quarter Report.

(d) Report the results of the mechanical properties *vs.* cycling capability of NCM-PVdF-based cells. (Sep. 10) **Complete**. See 4th Quarter Report.

Other work beyond the milestones.

To provide further insight to why electrodes fail, the group found a way to convert a coin cell into a three-electrode cell. Part of the process in making this cell required fabricating a new jig for our coin-cell assembly. Early attempts at this provided warnings as to the sensitivity of Li-ion chemistry to water intrusion. The slightest imperfection of the seal led to side reactions that occurred at greater than three times the rate of a well-sealed cell. It is believed that this is the first time a lab has produced a three-electrode cell that can be used for long-term cycling. As evidence, three coin cells were built from the same cathode and anode laminates. One of the cells was a typical two-electrode cell of graphite and NCM fabricated using the standard jig that came with the equipment; another cell was also a two-electrode cell assembled with a jig made in the LBNL machine shop; and the third cell consisted of three electrodes assembled using the LBNL jig. The cells were put on C/10 charge/discharge cycles between 3 and 4.3 V. Figure 1 shows the slippage of the cell capacity with each discharge relative to its previous discharge plotted *vs.* cycle number. Since this is a direct measure of the side reaction, and since the side reactions are very sensitive to contaminants, it was considered the most stringent test of our ability to make a well-sealed cell with three electrodes. As the figure shows, the difference in the rate of the side reactions is indistinguishable. (The cells made without a ref. electrode were temporarily taken off test at cycle 15 and then put back on test a week later.)

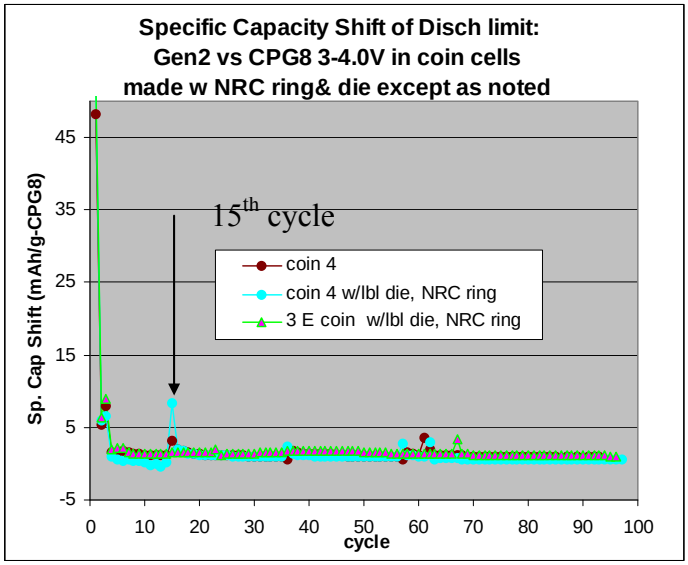

Figure 1. Three separate cells on test. Coin 4 is a cell made with original die and ring, Coin 4 w/lbl die was assembled with an LBL rig, and 3E coin was a three-electrode cell with the LBNL rig.

Following-up on last quarter's report, where it was indicated that the coulombic efficiency of the anode increased when the counter electrode was changed from Li to NCA, investigation of the coulombic efficiency of the cathode revealed no effect upon changing the anode from Li to graphite. This suggests that something about changing from a small to a large voltage difference is responsible for modifying the rate ot the side reactions in the cell.

TASK 1.2 - PI, INSTITUTION: Thomas Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – High-energy Density Cathodes and Anodes

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000 cycles/58 MWh).

OBJECTIVES: Synthesize and evaluate new electrode materials with improved energy density. Investigate the relationship of structure, morphology and performance of cathode and anode materials. Explore kinetic barriers, and utilize the knowledge gained to design and develop electrodes with improved energy density, rate performance and stability.

GENERAL APPROACH: Identify candidate electrode compositions by systematic analysis of phase diagrams and literature reports. Synthesize novel materials and/or unique structures and employ XRD, electron microscopy, vibrational spectroscopies, and electroanalytical techniques to determine their applicability to BATT goals. Characterize known and modified electrode materials (*e.g.,* non-olivine $LiMPO_4$) and establish correlations between crystal structure, morphology and performance. Provide guidelines for materials synthesis and electrode fabrication processes.

STATUS OCT 1. 2009: The solid-state chemistry of $LiMnPO_4$ has been found to differ significantly from that of $LiFePO_4$. Both structural and chemical instability are evident in the delithiated phase, with impacts on its utilization, rate capability, and possible, its safety. Solid solution behavior (Li_xMnPO_4 formation) in the vicinity of $MnPO_4$ contributes to isolation of domains within particles. Further, the oxidized material loses oxygen beginning below 150°C, generating substantial heat in the presence of electrolyte.

Convenient metathesis reactions involving lithium nitride have been found to produce lithium intermetallics or composites of ceramic nitrides with lithium or its alloys. These powders can be used to partially or fully prelithiate anodes containing carbon or other components.

EXPECTED STATUS SEP. 30, 2010: New 4-V class cathode materials will have been synthesized and their potential utility evaluated. A study of the relationships between cathode performance and particle morphologies will provide directions for increasing energy density through the use of micron-sized active materials with optimized microstructures. The effects of partial prelithiation of intermetallic anodes through metathesis will have been examined.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD).

MILESTONES:
(a) Report capacities and charge-discharge potentials for new cathode materials. (Mar. 10) **Complete**
(b) Report on reduction of anode irreversible capacities. (Jul. 10) **Complete**

PROGRESS TOWARD MILESTONES

Cathodes: Micron-sized, nanoporous, $LiFePO_4$/C spheres were synthesized by a single-step, ultrasonic, spray-pyrolysis method. The precursor solution, containing $Fe(NO_3)_3 \cdot 9H_2O$, $LiNO_3$, $NH_4H_2PO_4$, and citric acid, was formulated to produce gaseous products during droplet drying and subsequent reaction. The particles were characterized by their three-dimensional connected porosity (Fig. 1) and carbon-coated pores (Fig. 2). The total carbon content was *ca*. 7 wt%. XRD showed the active material to be phase pure and to have lattice parameters consistent with a low concentration of anti-site defects.

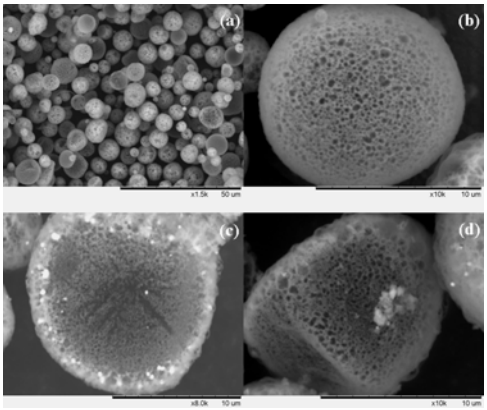

Figure 1. SEM images of a) 3D nanoporous $LiFePO_4$/C spheres; b) the surface of a single sphere; c, d) cross-sections of the spheres, showing the interconnected pores.

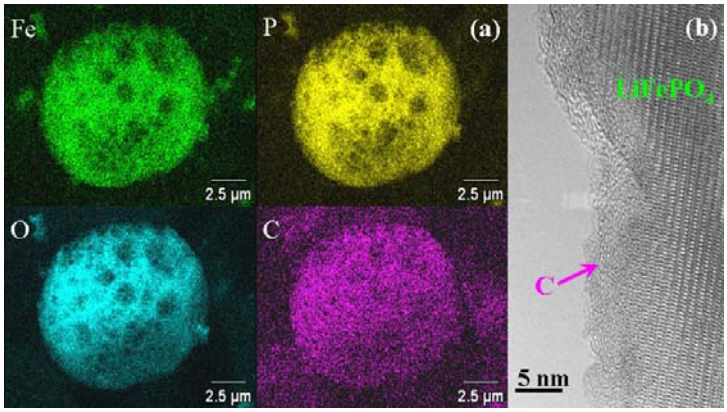

Figure 2. a) EDS maps of Fe, P, O, and C in a single 3D nanoporous $LiFePO_4$/C sphere; b) HRTEM image of the fracture surface showing the amorphous carbon layer.

The powder had excellent cyclability and good rate capability (Fig. 3). The conductive carbon coating and 3D, interconnected pore network, respectively, facilitated the kinetics of electron transport and Li-ion diffusion within the particles. The method is simple, fast, inexpensive, and scalable.

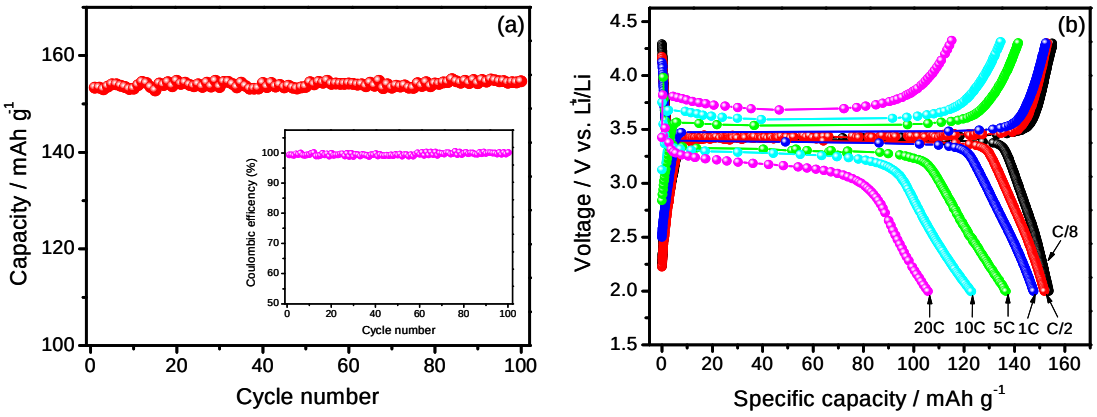

Figure 3. a) Cycling performance of nanoporous $LiFePO_4$/C at C/8; b) charge-discharge curves at various rates.

Efforts to prepare other cathode materials using this technique appear promising.

Collaborations: Chen, Kostecki, Liu, Doeff, Cabana, Srinivasan, NCEM, ALS, SSRL.

Presentation: "Visualization of Charge Distribution in Lithium Battery Electrodes," *61st Annual Meeting of the International Society of Electrochemistry*, Nice, France, September 28, 2010.

TASK 1.3 - PI, INSTITUTION: Karim Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Analysis - Interfacial Processes: SEI Formation and Stability on Cycling

SYSTEMS: Low-voltage, high-stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Low energy and poor cycle/calendar life

OBJECTIVES: Synthesis and evaluation of lithium manganese phosphate cathode material ($LiMnPO_4$) with improved electrochemical characteristics. Replace the graphite anode with an alternative anode material that meets the requirement for low cost and high energy. We will continue the development of binders for the cathode and alternative anode to understand and improve the properties of the SEI layer.

GENERAL APPROACH: Our approach is to develop an appropriate method to synthesis $LiMnPO_4$. The emphasis is to improve electrochemical performance with acceptable carbon content in the electrodes. The effect of particle size on the reversible capacity and cyclability will be investigated. Several binders with different mechanical properties will be investigated and evaluated with the alternative anode material. All materials will be tested electrochemically and provided to other researchers in the BATT program for evaluation. The coating processes for the new anode material will be optimized because they have different physical properties that, when combined with new binders, will influence the coating parameters.

STATUS OCT 1. 2009: We succeeded in synthesizing $LiMnPO_4$ by using solid-state and hydrothermal processes. The electrochemical performance is low for electrodes obtained by the hydrothermal process that yielded 0.250 μm particle size and that were carbon coated. However, when the particle size is to less than 100 nm, our studies showed an important impact on the electrochemical performance. The reversible capacity increased by a factor of 3. Modification of some parameters of the synthesis protocol will be made. In the anode side, high-reversible capacity was obtained with SiO_x:graphite, but cycling life still needs to be improved.

EXPECTED STATUS SEP. 30, 2010: Research will lead to improvement of the performance of $LiMnPO_4$. Other types of precursors used in the synthesis process will be explored and the performance will be compared after carbon coating in half cells. Due to the low cost and high capacity, the development of silicon-oxide-based anode material will continue. Different polyimide binders will be used in electrode development studies. The effect of these binders on the performance of the anode (first coulombic efficiency and reversible capacity) will be determined. Passivation related to SEI formation and the role of the polyimide binder will be studied and compared to that of water-dispersed binder.

RELEVANT USABC GOALS: High energy and low cost: 96 Wh/kg (PHEV, 40 miles). Cycle life, calendar life: 15 year life (at 40°C).

MILESTONES:
(a) Optimize a silicon-oxide composition with different carbon additives as anode material. (Feb. 10) **Complete**
(b) Study the effect of polyimide binders on SEI layer of the alternative anode. (Sep. 10) **Complete**
(c) Optimize synthesis method of $LiMnPO_4$ cathode material and its carbon coating process. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

During the last quarter, the cycling performance of a SiO_x:graphite anode at a 1:1 weight ratio was demonstrated. A stable reversible capacity of 780 mAh/g after 80 cycles at C/12 was achieved. However, at high rates, the anode's performance was negatively impacted by the large volume change of the particles. The effort then turned to analysis, starting with an examination of SiO_x:graphite anodes by *ex situ* and *in situ* SEM. Solid-polymer-based anodes were used as a means of avoiding solvent evaporation in the SEM chamber. The *ex situ* SEM analysis of the electrode surface, observed through the collector mesh holes, suggested that no change had occurred. However, *in situ* SEM of the electrode cross section showed the expansion/contraction of the SiO_x anode. The result (Fig. 1) revealed that the bigger particles (*ca*. 13µm) start to show cracks at around 0.1V during the lithiation process - fissures were observed as well as delamination from the current collector. During the delithiation process, all of the cracks remained - some fissures collapsed and others swelled. In general, it appeared that the smaller particles (< 2µ) did not crack. This result indicated that smaller particles and more elastic binders are needed for improved cycle life of SiOx:graphite electrodes.

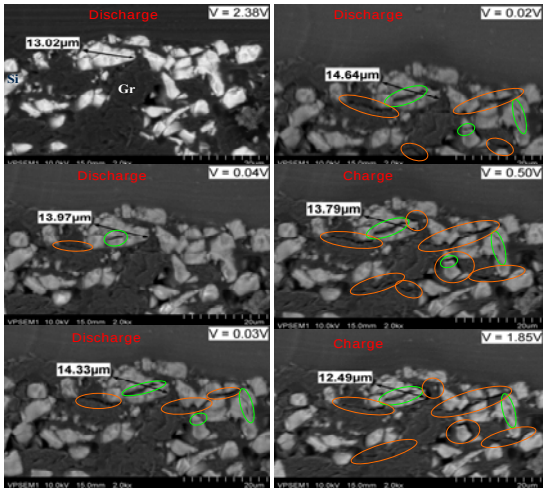

Figure 1. SEM images from *in situ* cycling test of Li/polymer/SiO_x:Gr (1:1) cell cross section.

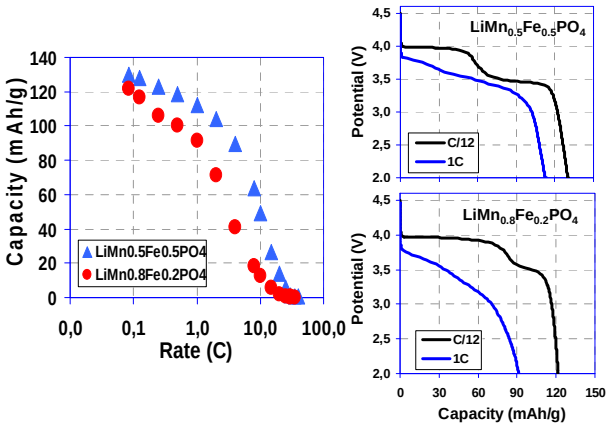

Figure 2. Rate capability of Li/$LiMn_{1-x}Fe_xPO_4$ cells in EC-DEC-$LiPF_6$, with x =0.2 and 0.5.

In the last quarter, it was observed that at low C rate the energy was highest in the range where Mn composition varied from 0.5 to 0.8 (*ca*. C/24). In this quarter, the rate capability of two cathode compositions of $LiMn_{1-x}Fe_xPO_4$, x = 0.2 and 0.5, were compared (Fig. 2). It was found that the active material with more Mn was more affected by the high rate - the drop in the Mn-plateau is more pronounced with higher discharge rate and higher Mn content. This result suggested that the composition limit, for power applications, should not exceed a Mn content of 0.5.

HQ is continuing its collaboration with members in the BATT Program: Vince Battaglia ($LiFePO_4$, graphite and LTO) and John Goodenough (discussion on the new oxide and olivine material).

TASK 1.4 - PI, INSTITUTION: Nancy Dudney, Oak Ridge National Laboratory

TASK TITLE – PROJECT: Cell Analysis - Investigations of Cathode Architecture Using Graphite Fibers and SEI-Coatings at Lithium and Graphite Anodes

SYSTEMS: Low-voltage, high-stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$
High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Poor cycle life. Poor abuse tolerance. Low energy density.

OBJECTIVES: Replace the Al sheet with highly-conductive graphite fibers as the skeleton and current collector for cathodes. Characterize the properties of synthetic SEI-like layers on Li and/or graphite anodes, including self-assembled monolayers (SAM) and inorganic films.

GENERAL APPROACH: Investigate cathode architectures based on a 3D skeleton of bonded graphite fibers. Look for improvement in the cycle life and thermal conductivity of the cathodes in the absence of organic binder and flaws related to stresses from processing. Study the interface of graphite particles and evaporated Li films with aprotic electrolytes, investigating the performance of synthetic layers prepared by dip or vapor coating. Determine the interface impedance and current-voltage behavior as well as irreversible capacity loss and fade upon extended cycling.

STATUS OCT. 1, 2009: Composites of $LiFePO_4$ and conductive carbon fibers formed by thermal processing have been shown to have promising cycle life and capacity utilization. Energy and power performance have been compared for cathodes with different thickness, loading of active material, and architectures. Thermal transport studies of the carbon composites have been initiated. Approximate costs of several commercial and prototype carbon fibers have been evaluated. Studies of native SEI formed at a smooth equilibrium Li surface in contact with the organic carbonate electrolyte solutions have identified non-linear current-voltage behavior that differs from Butler-Volmer kinetics for both cathodic and anodic currents. No significant effect has been found from the vinylene carbonate electrolyte additive.

EXPECTED STATUS SEP. 30, 2010: Efforts to understand how SEI formation influences Li roughening will be redirected to the synthesis and properties of synthetic coatings on graphite or Li. Several SAMs will be prepared and evaluated at Gr/electrolyte or Li/electrolyte interfaces. Lipon will also be evaluated as a potential coating for graphite particles. Initial characterization of the coated anodes will focus on capacity retention, cycle life, and power performance. Experiments will be conducted to understand Li^+ transport through the SAM by varying the molecular structure. Binder-free composite cathodes of carbon fibers and $LiFePO_4$ or $LiNi_xMn_xCo_{1-2x}O_2$ will be prepared for assembly in pouch cells at LBNL. Efforts will focus on increasing the capacity/area and identifying methods to form robust tabs.

RELEVANT USABC GOALS: Available energy 11.6kWh at 10kW rate, 5000 charge depleting cycles, and energy efficiency of 90%.

MILESTONES:
(a) Provide composite cathodes of $LiFePO_4$ and carbon fibers compatible with pouch cell assembly. (Apr. 10) **Coordinating with V. Battaglia, LBNL**
(b) Form and evaluate self assembled monolayer or Lipon glass coatings on lithium and/or graphite anodes. (Sep. 10) **Complete.**

PROGRESS TOWARD MILESTONES

Cathodes with carbon fibers

$LiFePO_4$ cathodes were prepared with carbon pitch and conductive carbon fibers at 700ºC, as was done with earlier composites, but these cathodes were prepared with loose fibers. Loose fibers should allow for better control of the density, loading, and cathode thickness. Cycled in half cells, these composites possessed the same good cycle life, approached the theoretical energy, and had better power than reported earlier for composites using the Toray carbon paper. As shown in Fig. 1, half of the capacity was realized for a 10C discharge. Earlier work with Toray carbon fiber papers was published in JES. A metallization method to prepare the fibers for pouch-cell fabrication was also developed.

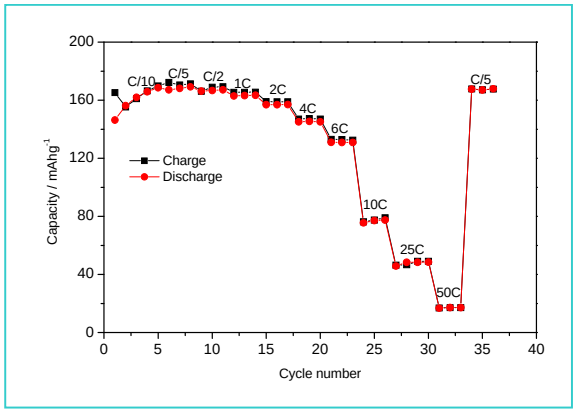

Figure 1.

Thermophysical studies comparing $LiFePO_4$ + carbonized mesophase pitch to the standard binder + carbon black additives were conducted in collaboration with researchers at the ORNL High Temperature Materials Lab. The specific heat capacity of $LiFePO_4$ up to 500ºC was determined, apparently for the first time (Fig. 2). Results deviated somewhat from the ideal Debye behavior (to be verified with an alternative source of powder). The effect of replacing PVDF and carbon black (15 to 20 wt%) with carbonized mesophase pitch (*ca*. 5 wt%) was determined by measuring the heat capacity and thermal conductance of pressed pellets of the same porosity. Properties were measured to 150º, and to 500ºC for the binder-free samples. Pellets with the pitch binder had slightly lower heat capacity, but about two-fold higher thermal diffusivity. Thermal and electronic characterization of the heat-treated pitch were also initiated, but were complicated by the foaming action that starts at 350ºC.

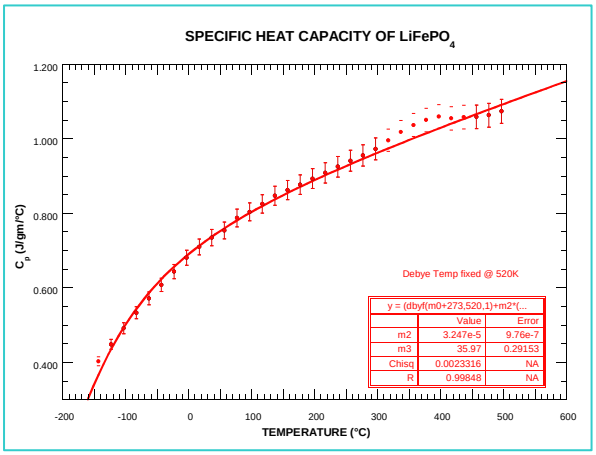

Figure 2.

Lipon glass coatings for lithium metal or graphite anodes:

XPS results added further evidence that thin Lipon films (up to 80nm) deposited onto both graphite powders and prefabricated graphite electrode sheets had little effect on reducing the formation of the SEI layer in $LiPF_6$ carbonate electrolytes. Lipon films also did not protect the graphite anodes in EC-free, PC electrolytes. These results were surprising as Lipon is known to be a dense solid-electrolyte material when applied to a variety of surfaces and as such should have prevented the electrochemical reduction of the solvent. From all indications, the Lipon films completely coated the graphite surfaces with the expected thickness and remained in place when in contact with the electrolyte. An outstanding issue is to demonstrate that the film is electronically resistive when deposited onto carbon. This research was presented at the October ECS meeting; publication of this effort will complete milestone (b).

TASK 1.5 - PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Cell Analysis – New Electrode Design for Ultrahigh Energy Density

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_xCo_{1-2x}Mn_xO_2$
Low-voltage, high-stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: High energy system: low energy, poor cycle life

OBJECTIVES: Develop a scalable, high-density, binder-free, low-tortuosity electrode design and fabrication process to enable increased cell-level energy density for a range of active materials compared to conventional Li-ion technology.

GENERAL APPROACH: Develop fabrication methods for high density sintered cathodes and anodes with controlled pore volume fraction and pore topology. Electrochemically test electrodes in laboratory half-cells and small lithium ion cells (<100 mAh), and model electrode response. Aim to increase cell-level specific energy and energy density by maximizing electrode density and thickness, under operating conditions commensurate with USABC targets for PHEV and EV.

STATUS OCT. 1, 2009: This is a new project initiated May 1, 2010.

EXPECTED STATUS SEP. 30, 2010: First tailored-porosity sintered $LiCoO_2$ electrodes fabricated by freeze-casting will have been made and tested.

RELEVANT USABC GOALS: EV: 200 Wh/kg; 1000 cycles (80% DoD).

MILESTONES: This is a new project in FY 2010.
(a) Report fabrication procedure, structural characterization, and initial electrochemical test data for directional freeze-cast and sintered $LiCoO_2$ electrodes in laboratory scale lithium half-cells. (Sep. 10)

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PROGRESS TOWARD MILESTONE

Collaborator: Antoni P. Tomsia (LBNL)

Accomplishments: During the past quarter, MIT provided $LiCoO_2$ powders and sintering-heat-treatment conditions to collaborators at LBNL, who produced the first directionally-freeze-cast electrodes for electrochemical testing at MIT. The starting powder was a Seimi $LiCoO_2$ that was jet-milled to produce a d_{50} of 3.44 μm. Three samples were prepared by freeze casting, having solids loading prior to sintering of 10, 20 and 30% by volume. All were subjected to the same sintering-heat-treatment and produced sintered densities of 26.7, 37.5, and 55.6%, respectively. As show in Fig. 1, the directional-freeze-drying process produced an oriented microstructure with aligned, low-tortuosity porosity, as was desired. With increasing sintered density, there was a higher density of lateral "arms" in the dendritic structure, which, in the highest density sample, appeared to be obstructing the oriented porosity.

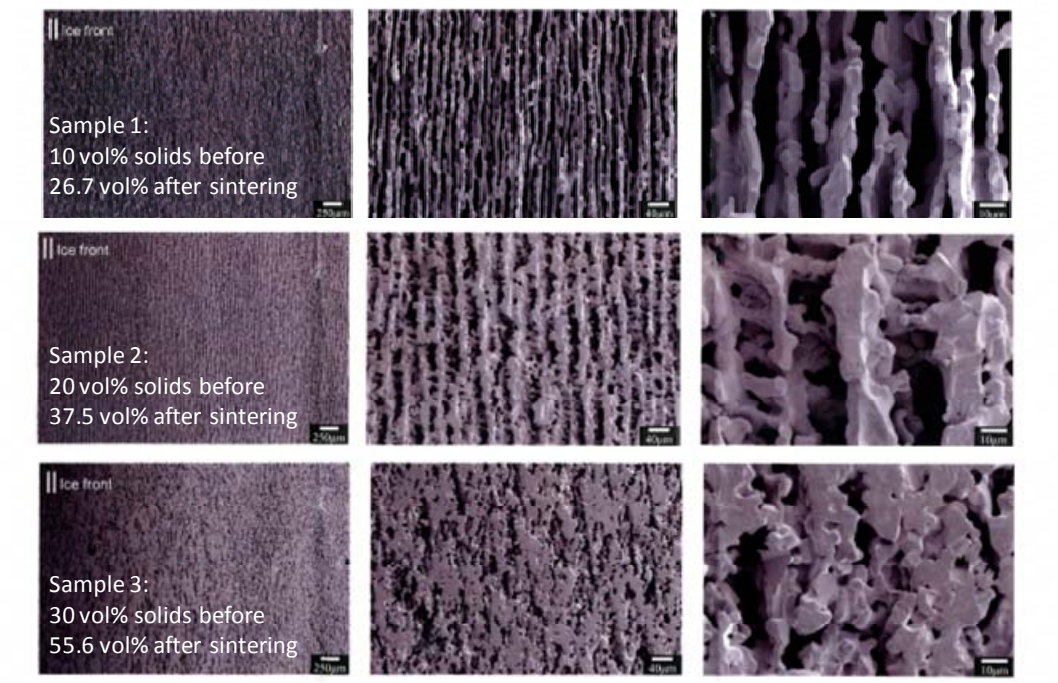


Figure 1. Cross-sections of directionally freeze-cast and sintered $LiCoO_2$ electrodes, viewed parallel to the solidifying ice front. The volume percentage of solids before and after sintering is indicated in each case. Unidirectionally oriented pore channels are produced.

Samples 2 and 3 were sectioned into electrodes for electrochemical testing in Swagelok™ cells (the lowest density sample did not have sufficient structural integrity for sectioning). Figure 2 shows galvanostatic test data in which the improvement in capacity retention for Sample 2, at 1C rate and higher, is evident. This is attributed to a reduced incidence of pore channel blocking compared to Sample 3.

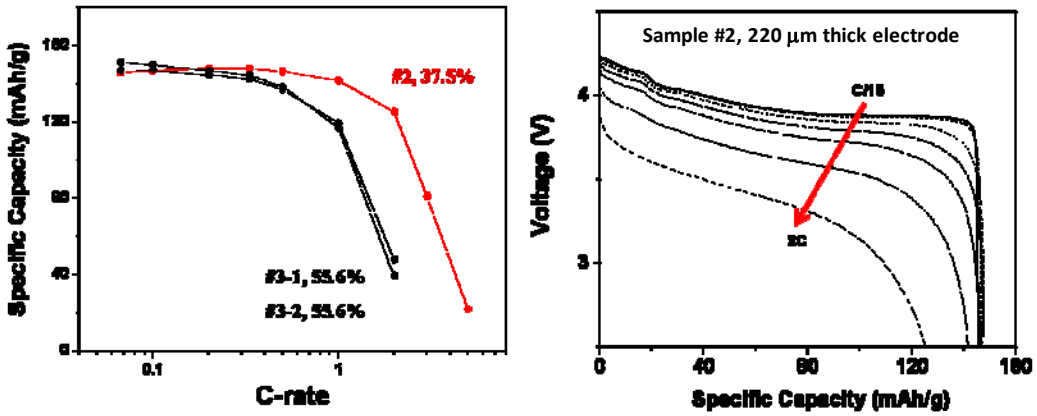


Figure 2. Galvanostatic test results showing discharge capacity *vs*. C-rate for samples 2 and 3, measured on electrodes of 220 µm thickness.

These preliminary results show that binder-free, conductive-additive-free, sintered electrodes can be successfully fabricated using the directional freeze-drying process. They also suggest that the dendrite morphology, which is a function of the sample formulation and freeze-drying conditions, is important to the final pore-channel microstructure. In addition to the freeze-casting parameters, the sintering conditions affect final sintered density and pore topology. Future work will examine the interplay of these process parameters, with the objective of obtaining higher sintered densities while retaining unobstructed, unidirectional porosity.

BATT TASK 2
ANODES

TASK STATUS REPORT

Task 2.1 - PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE: Anodes: Novel Anode Materials

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High voltage, high power: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiMn_2O_4$

BARRIERS: Low energy, poor low-temperature operation, and abuse tolerance limitations

OBJECTIVES: 1) Replace graphite with an alternative, inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. 2) Improve the capacity and cycle-life limitations of intermetallic electrodes and their abuse tolerance in cells.

GENERAL APPROACH: Our approach is to search for inexpensive anode materials that provide an electrochemical potential at least a few hundred mV above the potential of metallic Li. We will focus predominantly on Sn- and Si-based systems as well as metal oxides. A major thrust of our research is to design new electrode architectures (by electrodeposition techniques) in which a Cu foam provides an electronically connected substrate onto which electrochemically active metals can be deposited. As a new initiative for FY2010, we plan to exploit an autogenic technique to fabricate carbon-coated anode materials as well as new forms of carbon.

STATUS OCT 1. 2009: Significant progress was made in increasing the reversible capacity of Cu_6Sn_5 electrodes by electrodepositing Cu and Sn onto Cu-foam electrodes (also fabricated by electrodeposition). Our search for new Sn-based intermetallic electrodes led to a study of $LaSn_3$, which was completed and published. Investigations of nanoparticulate Si-C and carbon-coated TiO_2 electrodes had been initiated.

EXPECTED STATUS SEP. 30, 2010: Three-dimensional architectures of Si and intermetallic electrodes will have been designed to improve their electrochemical properties. Several electrode materials will have been prepared by a dry autogenic reaction, which are expected to include carbon-coated Si, Sn-based compounds, and various metal oxides.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:
(a) Complete a study of carbon-coated TiO_2 electrodes. (Apr. 10) **Complete**
(b) Prepare metal and intermetallic electrode architectures by electrodeposition and determine their electrochemical properties in lithium half cells and full cells. (Sep. 10) **Complete**
(c) Exploit an autogenic process for synthesizing and simultaneously coating Si, Sn, and metal oxides with carbon and evaluate the materials for their electrochemical properties. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Collaborators: J.T. Vaughey (Co-PI), Lynn Trahey, B. Polzin, M. D. Slater (Argonne)
Milestone addressed: (b) Prepare metal and intermetallic electrode architectures by electrodeposition and determine their electrochemical properties in lithium cells.

Accomplishments

All three milestones were completed with respect to FY 2010 goals. Milestone (b) is being extended into FY 2011 as part of the newly awarded Anode project (Sept. 2011).

This past quarter saw the continuation of our investigation of porous Cu-foam current collectors as substrates for Sn and Cu-Sn anodes. An electroless Sn-deposition method to plate Sn on porous Cu foams of '90 pores per inch', supplied by Circuit Foil, was evaluated. The foams were calendered to a thickness of 100 microns for evaluation in coin cells. The calendering resulted in a substantial loss of porosity (Fig. 1).

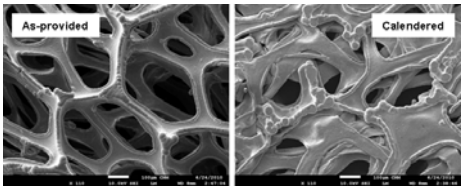


Figure 1. Copper foams, provided by Circuit Foil (left) and after calendaring (right)

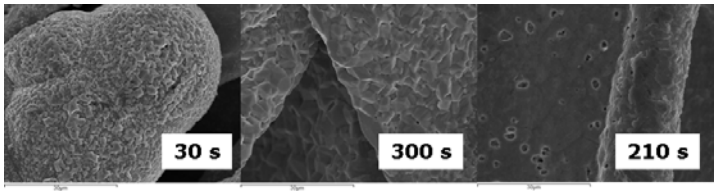


Figure 2. SEM images of tin-coated copper foam (a) and (b) after deposition times of 30 s and 300 s, respectively (Method 2), and (c) after 210 s (Method 1).

Copper foams were coated with Sn using an immersion, electroless-plating bath by two methods: Method 1) coating the foil and then calendering, and Method 2) coating the foam after calendaring. Several immersion times were evaluated, the goal being to establish an optimum Sn thickness to achieve stability to lithiation and delithiation on long-term cycling. Figures 2a and 2b show SEM images of Sn-plated Cu foams by Method 2 using immersion times of 30 and 300 seconds, respectively; the resulting morphology showed that Sn deposition was conformal and successfully filled the pores. For Method 1, non-calendered foams were plated with Sn for 210 seconds, and then calendered to 100 microns (Fig. 2c). In this case, the morphology of the Sn was considerably flatter compared to that obtained with Method 2, which was attributed more to differences in surface area rather than to the calendaring process. It is anticipated that the starting morphology, crystallinity, and thickness of the electrodeposited Sn will strongly influence cycle life; these parameters will be evaluated in more detail in the newly awarded Anode project for FY 2011.

Half-cell cycling data of Sn-coated Cu foams produced by Method 2 with a 120 second Sn immersion time (thin) and an identical foam with a plating of thicker, more dendritic Sn are shown in Fig. 3. Gen 2 electrolyte was used. Because the mass of deposited Sn is difficult to determine, the data were normalized to the discharge capacity on the 3rd cycle, by which time the SEI was largely formed. The thinner, conformal coating of Sn provides superior capacity and cycling behavior than the thicker, more dendritic Sn electrodes, as anticipated.

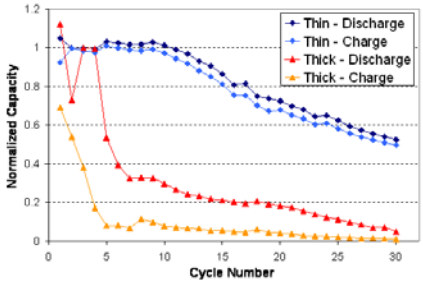


Figure 3. Half-cell cycling data of tin-coated copper foams produced by Method 2.

TASK 2.2 - PI, INSTITUTION: M. Stanley Whittingham, Binghamton University

TASK TITLE - PROJECT: Anodes - Anodes: Novel Materials

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Cost, safety, and volumetric capacity limitations of Li-ion batteries

OBJECTIVE: To replace the presently used carbon anodes with safer materials that will be compatible with low -cost layered oxide and phosphate cathodes and the associated electrolyte.

GENERAL APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites from bulk to nano-size. We will learn from an understanding of the tin-cobalt anode, the only commercial anode besides carbon, why amorphous nanomaterials work. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal, kinetic and structural stability to gain an understanding of their behavior.

STATUS OCT 1. 2009: We have shown that bulk crystalline metals have a high capacity, react readily with Li but their capacity faded rapidly after several deep cycles in carbonate-based electrolytes; and that their behavior was no better under shallow cycling. We have shown in contrast that amorphous nano-size Sn alloys, unlike pure Sn, have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like Co. We have also shown that nano-size manganese oxides, unlike crystalline vanadium and manganese oxides, are possible anode candidates when SEI formers such as LiBOB are added to the electrolyte.

EXPECTED STATUS SEP. 30, 2010: From our program to understand capacity fade of Sn and Sn compounds on cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of Sn morphology on capacity fade, and to have improved the electrochemical performance of the materials identified. Specifically we will know how the nanostructure of Sn and Si impacts cycle life, and how composites impact capacity and cycle life. We will have some clues as to how to control the SEI on such materials to optimize life.

RELEVANT USABC GOALS: 5000 deep discharge cycles, abuse tolerance to cell overcharge and short circuit, and minimum system volume.

MILESTONES:
(a) Determine the limitations, besides cost, of the Sn-Co-C nanostructured anode. (Mar. 10) **Complete; utilizing knowledge gained to find new nano-amorphous materials.**
(b) Explore nano-size tin/silicon alloys and metal oxides to identify their cycling characteristics. (Sep. 10) **1st phase complete**
(c) Explore cobalt-free alloys to identify lithium active stable phases. (Sept. 10) **1st phase complete**
(d) Identify the structural and surface changes of tin containing anodes during cycling working collaboratively with LBNL. (Sep. 10) **Complete – pure carbonates cannot be used**

PROGRESS TOWARD MILESTONES

Development of novel anode materials continued to be the focus this quarter. It has previously been shown that the amorphous Sn-based anode has excellent capacity retention due to a stable SEI layer formed on the nano-structured particles. In this quarter, a high capacity nano-Si based anode material demonstrating similar behavior is reported.

Carbon-coated Si was synthesized by an *in situ* reduction method. Figure 1 shows the cycling behavior of this material. The nano-Si-C electrode was discharged and charged at 0.3 mA/cm^2 in the first cycle to help form a surface interlayer. Then the current density was increased to 0.5 mA/cm^2. In the first cycle, the reversible capacity reached as high as 970 mAh/g; for the following 25 cycles, the capacity stayed above 800 mAh/g, which is more than twice the capacity of graphite. Figure 1 gives the charge-discharge profile. The overlapping curves indicate that the capacity cycling was highly reversible. The coulombic efficiency is shown in Fig. 2 (top). It increased from 74% in the first cycle to 99.7% in the 10th cycle and stayed around 100.0% in the following cycles, as indicated in the insert. This suggested that the surface layer (SEI) formed on the Si anode was highly stable and protective. This test of Si included an additive in the EC/DMC electrolyte. Work is now continuing on other impacts of the additive; the results will be discussed next quarter.

The anode study is a collaboration with R. Kostecki (LBNL) and P. Chupas (ANL).

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

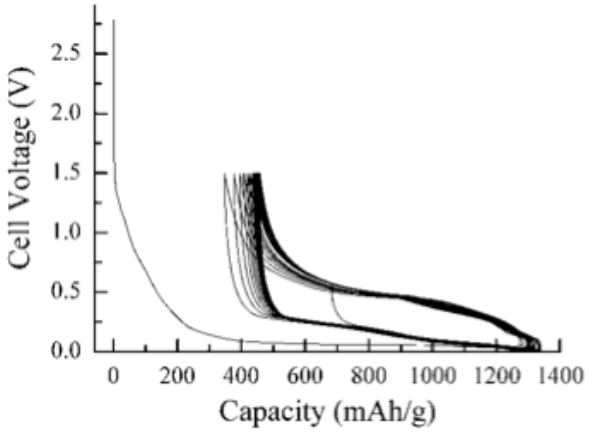


Figure 1. Electrochemical cycling of nano-Si-C anode between 0.01 and 1.5 V at 0.5 mA/cm^2 after the first full cycle. The first cycle was 0.3 mA/cm^2.

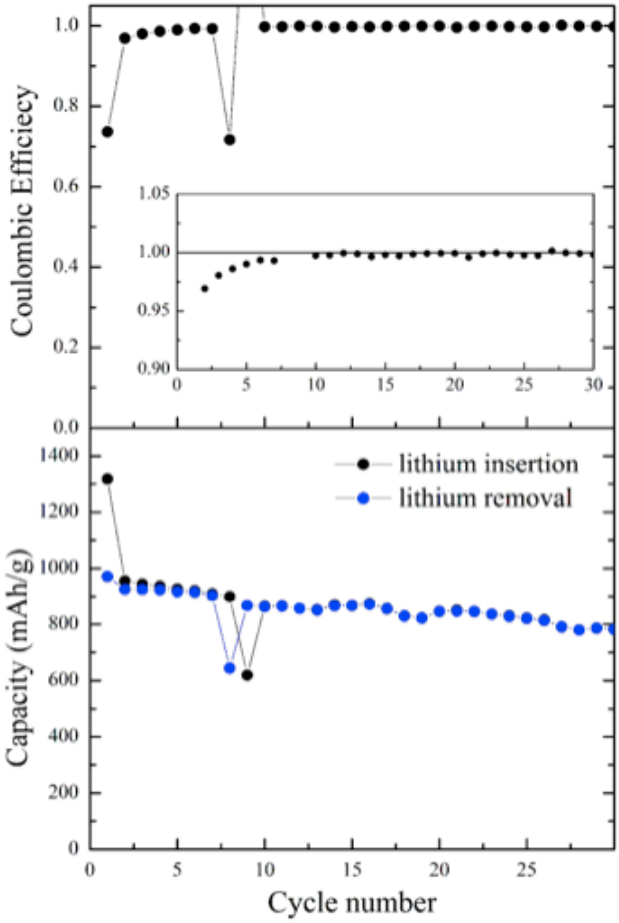


Figure 2. (top) The coulombic efficiency of cycling and (bottom) the capacity on both lithium insertion and removal, of the data shown in Fig. 1.

TASK 2.3 - PI, INSTITUTION: Prashant N. Kumta, University of Pittsburgh

TASK TITLE - PROJECT: Anodes - Nano-scale Composite Hetero-structures: Novel High Capacity Reversible Anodes for Lithium-ion Batteries

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Low specific energy and energy density, poor cycle life, large irreversible loss, poor rate capability, and calendar life.

OBJECTIVES: To identify new alternative nanostructured anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The objective is to replace carbon with an inexpensive nanostructured composite anode material that will exhibit higher capacity in comparison to carbon while exhibiting similar irreversible loss, and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, and cycle life limitations of silicon-based electrodes as well as the irreversible loss.

GENERAL APPROACH: Our approach is to search for inexpensive silicon- and carbon-based composite electrodes (powders rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of metallic Li, and 2) a capacity of at least 1000 mAh/g or greater (>2200 mAh/ml). We will focus on exploring novel, low-cost methods to generate nanoscale heterostructures of various Si nanostructures and different carbon forms derived from graphitic carbon, and nanotubes (CNT). Other electrochemically inactive matrices will also be explored. Promising electrodes will be evaluated in half cells against metallic Li and compared to graphite as well as full cells. Electrode structure, microstructure, rate capability, long- and short-term cyclability, as well as the origin and state of the SEI layers, will be explored.

STATUS OCT 1. 2009: Nano-scale electrode powders comprising Si-graphitic carbon-polymer derived carbon, and CNT-related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C structures exhibit stable capacities of 700-1000 mAh/g.

EXPECTED STATUS SEP. 30, 2010: Efforts will continue to generate nano-composite 'core-shell' and aligned structures of Si nanowires, nanorods, and nanotubes, and C nanotubes exhibiting capacities higher than 1000 mAh/g. Research will be conducted to study the synthesis conditions, the nano-scale microstructure affecting the energy density, rate capability, origin of the irreversible loss, and to characterize the SEI layer and outline methods to reduce irreversible loss.

RELEVANT USABC GOALS: Available energy for CD Mode, 10 kW Rate: 3.4 kWh (10 mile) and 11.6 kWh (40 mile); Available Energy for CS Mode: 0.5 kWh (10 mile) and 0.3 kWh (40 mile); 10s peak pulse discharge power: 45 kW (10 mile) and 38 kW (40 mile); Peak Regen Pulse Power (10 sec): 30 kW (10 mile) and 25 kW (40 mile); Cold cranking power at -30^{o}C, 2sec-3 Pulses: 7kW; Calendar life: 15 years (at 40^{o}C); CS HEV Cycle Life, 50 Wh Profile: 300,000 Cycles

MILESTONES:
(a) Report reversible capacity *vs*. the target of 1000 mAh/g. (Mar. 10) **Complete**
(b) Reduce the first-cycle irreversible capacity loss to less than 20%. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

In Q3, the use of high-energy mechanical milling (HEMM), a low-cost and large-scale manufacturing process was reported. The process resulted in the synthesis of amorphous Si + C composite (*a*-Si/C) as well as *nc*-Si + C composite (*nc*-Si/C) in powder form with a structural architecture similar to thin film *a*-Si/C. In this report, the electrochemical results of *a*-Si/C and *nc*-Si/C composites are discussed. The variation of specific capacity *vs*. cycle number of *a*-Si/C composite for 50 cycles at C/3 rate, Fig. 1, showed a 1st cycle discharge capacity of *ca*. 1400 mAh/g and 1st cycle charge capacity of *ca*. 1000 mAh/g, which equates to an irreversible loss *ca*. 28%. This material showed excellent long-term capacity retention with a 0.12% per cycle fade to 50 cycles. On the other hand, the electrochemical results of *nc*-Si/C composite, Fig. 2, showed a 1st-cycle discharge capacity *ca*. 1400 mAh/g and 1st-cycle charge capacity *ca*. 1200 mAh/g which is an irreversible loss of only *ca*. 10%. It is interesting to note that the 1st-cycle irreversible loss of *nc*-Si/C was much lower compared to *a*-Si/C composite and comparable to pure *a*-Si (*ca*. 9 to 12%). The *nc*-Si/C composite also showed excellent cyclability up to 100 cycles with a 0.19%/cycle fade. The above results clearly suggest that the Si/C composite synthesized by ball milling of amorphous Si and graphite in the presence of PAN followed by thermal treatment to a suitable temperature produces a material for a promising Li-ion anode exhibiting high reversible capacity and excellent stability in comparison to microcrystalline Si/C composites that show higher fade in capacity (0.4 to 0.7%) per cycle.

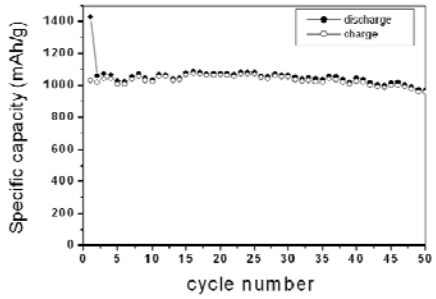


Figure 1. Variation of specific capacity *vs*. cycle numbers of *a*-Si/C cycled at C/3 rate.

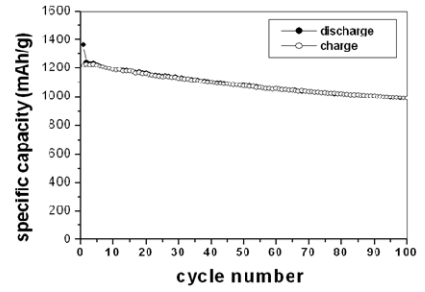


Figure 2. Variation of specific capacity *vs*. cycle numbers of *nc*-Si/C composite cycled at C/7 rate.

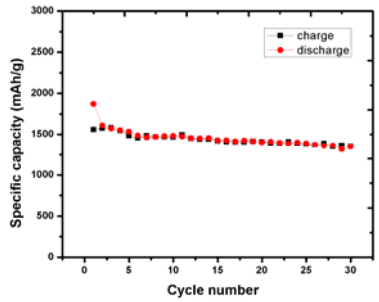


Figure 3. Variation of specific capacity *vs*. cycle numbers of *nc-Si/CNT on Inconel* cycled at C/15 rate.

In other work, the electrochemical performance of *nc*-Si deposited on vertically aligned carbon nanotubes (CNTs) grown on INCONEL 600 alloy was studied using a direct, simple, liquid-injection, CVD approach. The synthesized nanostructured "binder-less" and "additive-less" electrode directly tested in a half-cell showed a low irreversible loss of only 16% and a first discharge capacity of 1870 mAh/g when cycled at *ca*. C/15. Further, the fade in capacity was *ca*. 0.5%/cycle and capacity retention was *ca*. 1350 mAh/g after the 30th cycle, indicating a promising future for this technique.

Attempts to Meet Expected Sept. 30, 2010 Status: In FY 2010, the following target milestones were achieved: 1) reversible capacity above 1000 mAh/g and 2) 1st-cycle irreversible loss below ~20%. Nanocomposites of *nc*-Si droplets deposited on CNTs using the simple CVD method helped attain very high reversible capacity (above 1500 mAh/g) with excellent capacity retention and low irreversible loss (below 20%) due to the interfacial C layer and reduced surface area of CNT by Si coverage. In addition, *a*-Si/C and *nc*-Si/C composites that exhibited high reversible capacity (*ca*. 1000 to 1500 mAh/g) with excellent capacity retention (0.1 to 0.2% per cycle) were synthesized by a cost effective HEMM process.

TASK 2.4 - PI, INSTITUTION: John B. Goodenough, The University of Texas at Austin

TASK TITLE – PROJECT: Anodes - Solid Electrolyte Batteries

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

OBJECTIVE: To evaluate alternative material configurations.

GENERAL APPROACH: Goals: To explore use of a solid Li^+-ion electrolyte that blocks dendrite penetration to the cathode and allows different liquid electrolytes in contact with solid electrodes or O_2-reduction catalysts of an air cathode.

A solid Li^+-ion electrolyte having a Li^+-ion conductivity $\sigma > 10^{-3}$/S/cm at room temperature would allow use of an aqueous electrolyte on the cathode side containing a soluble species having a redox couple with a current collector, *e.g.,* $Cu(NO_3)_2/Cu$. Such a liquid cathode would give a flat voltage profile and could have a much larger capacity than any that has been achieved with an insertion-compound cathode. Since a Li/air battery also uses a solid Li^+-ion electrolyte, comparisons with what can be achieved with a Li/air cell are relevant.

STATUS OCT. 1, 2009: We have constructed a cell consisting of different metals M_1 and M_2 as the anode and cathode of a cell having a LISICON separator and a non-aqueous electrolyte on one side, an aqueous electrolyte on the other. We used this cell to evaluate the energy density, rate of charge/discharge, cycle life, and feasibility of large-scale manufacture.

EXPECTED STATUS SEP. 30, 2010:

- The redox couples and metals M_1 and M_2 of a M_2/Liq./LISICON/Liq./ M_1 Li^+-ion battery will have been optimized and its commercial viability *vs.* existing Li^+-ion batteries will have been evaluated.
- The performance of the cells will have been compared with that of a Li/Air cell.

RELEVANT USABC GOALS: Available energy > 80 Wh/kg, 5000 deep-discharge cycles, 15-year calendar life. *Note:* Fast discharge may depend on an associated electrochemical capacitor if the battery stores a large amount of energy,

MILESTONES:
(a) Develop and test a suitable Li/air test cell. (Jan. 10) **Complete**
(b) Optimize components of the cell. (Apr. 10) **Complete**
(c) Develop a Li/Air cell (Jul. 10) **Complete**
(d) Test alternative cathode catalysts (Sep. 10) **On going, delayed to Mar. 11**
(e) Compare the performance test cells with that of the best reported Li/air cell (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

In our second quarterly report, an 'aqueous electrode' concept was demonstrated through a prototype Li|$Fe(NO_3)_3$(aq) battery. Several drops of $Fe(NO_3)_3$ solution resulted in a Li|$Fe(NO_3)_3$(aq) battery that discharged at 3.8 V and charged at 4.2 V, which provides a higher energy efficiency (EE) than that of today's Li/Air cell. However, the Li|$Fe(NO_3)_3$(aq) battery showed a different behavior in subsequent experiments in which the cathode side was closed.

Figure 1 displays the discharge/charge curves of the closed-cathode Li|$Fe(NO_3)_3$(aq) battery. The battery used Li metal as its anode and 2 molar $Fe(NO_3)_3$ solution as its cathode. A commercial solid electrolyte, $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$, was used to separate the anode from the cathode. The open circuit potential (OCP) of the battery was 3.99 V. When a current of 0.50 mA was applied to the battery, its potential dropped to 3.74 V. The difference of 0.25 V is due to the low conductivity of the solid electrolyte as compared to carbonate-based electrolytes. Unlike the very flat plateau shown in the discharge curve of the 'open-cathode' Li|$Fe(NO_3)_3$(aq) battery, the discharge curve of the present battery slowly decreased with time to 2.80 V from 3.74 V. On charge, the potential of the battery reached 4.73 V rather than holding at 4.20 V. The approximate 1.0 V discrepancy between the discharge/charge curves indicated that the 'closed-cathode' Li|$Fe(NO_3)_3$(aq) battery showed a poorer performance than the 'open cathode' Li|$Fe(NO_3)_3$(aq) battery. Moreover, the battery with the 'open-cathode' had no irreversibility.

After the battery was charged, the cathode solution was collected and a precipitate found. $Fe(NO_3)_3$ is susceptible to hydrolysis in aqueous solutions. According to its solubility product, the pH of the solution depends upon the $Fe(NO_3)_3$ concentration, as shown in Fig. 1b. If the $Fe(NO_3)_3$ solution concentration is 2 molar, the solution pH is 1.1. But the solution pH changes to 5.7 if the Fe^{3+} is totally reduced to Fe^{2+} in the discharge process. The change in pH results in the precipitation of FeO(OH) (pH=2.0) and $Fe(OH)_3$ (pH=4.48). The precipitate not only decreases the concentration of the active compound in solution and lowers the capacity, it also covers the surface of the solid electrolyte to increase its resistance. Therefore, another aqueous redox couple is being pursued to replace the $Fe(NO_3)_3/Fe(NO_3)_2$ in order to improve the performance of the aqueous electrode in the Li battery.

Work on a garnet solid electrolyte in place of an alternative cathode catalyst for the Li/Air cell was also initiated this quarter.

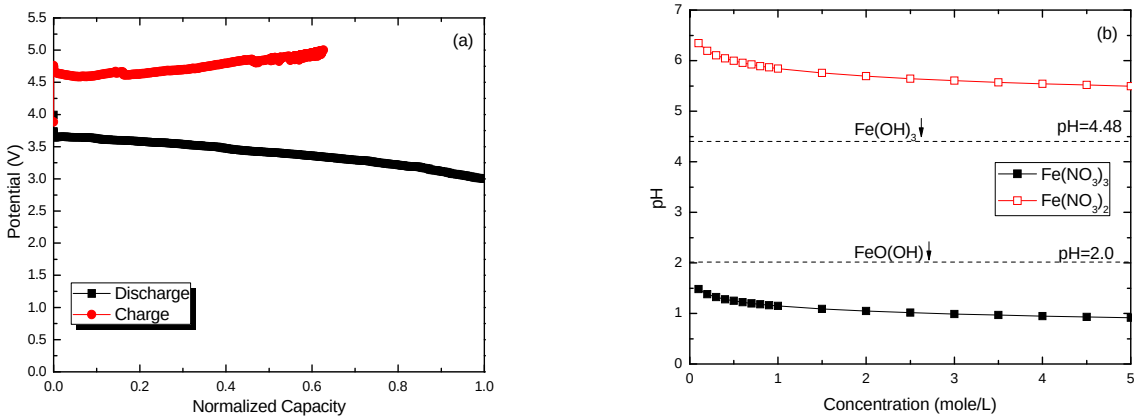


Figure 1. (a) Discharge/charge curves of Li|$Fe(NO_3)_3$ battery; (b) Hydrolysis of the $Fe(NO_3)_3$ and $Fe(NO_3)_2$ in aqueous solution.

Collaboration this quarter: Karim Zaghib, Hydro-Québec.

TASK 2.5 - PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE – PROJECT: Anodes – Development of High Capacity Anode Materials

SYSTEMS: High voltage, high power: Graphite/1 M $LiPF_6$ in EC:DEC 1:2/$LiMn_2O_4$
Low-voltage, high stability: Graphite/1 M $LiPF_6$ in EC:DEC 1:2/$LiFePO_4$

BARRIERS: Low energy density, cost, poor cycle life and large irreversible capacity

OBJECTIVES: To develop high capacity, low cost anode with good rate capability to replace graphite in Li-ion batteries.

GENERAL APPROACH: Our approach is to manipulate the nano-structure and conductivity of Si and SnO_2 to improve their mechanical and electrical stability. Both nano-sized and micro-sized Si particles with nano-pore structures have been investigated. The electronic conductivity of silicon particles will be improved by CVD-coated carbon. Self-assembled templating method will be used to incorporate silicon particles into graphene sheet to improve the electronic conductivities between Si particles and accommodate the volume variation of Si during cycling.

STATUS OCT. 1, 2009: Project initiated Jan. 1, 2010. Highly stable, free standing SnO_2/graphene and TiO_2/graphene paper electrodes were successfully prepared through a unique self-assembly approach. These free standing paper electrodes can operate with no extra current collector and conductive additive. Nano-TiO_2/Graphene composite has demonstrated a capacity of ~170 mAh/g at 1C rate. SnO_2/graphene composite also demonstrated a capacity of ~790 mAh/g. Stable cycling and excellent rate capability were achieved in both composites. Nano Si and micro-sized Si particles with nano-porosity were coated with carbon by CVD process and investigated for their anode applications.

EXPECTED STATUS SEP. 30, 2010: Improve the cycling stability of Si based anode. Minimize the initial irreversible capacity loss of Si-based electrode by adjusting the mesopore volume of carbon additives. Alternative conductive binders will also be investigated to maintain a strong bonding with Si during cycling. The composition and cycling protocols of Si/graphene hybrid electrode will be optimized to balance the high capacity and cycling stability.

RELEVANT USABC GOALS: > 96 Wh/kg (PHEVs), 5000 deep-discharge cycles, 15-year calendar life, and improved abuse tolerance.

MILESTONES:
(a) Use CVD-coated carbon on Si surface to improve the electronic conductivity of individual Si particles (Mar. 10). **Complete**
(b) Develop composite anode based on Si/Ketjenblack carbon with high mesopore volume to accommodate the volume expansion of Si during cycling. (Mar. 10) **Complete**
(c) Optimize Si/graphene hybrid anode material and improve their cycling stabilities (Sep. 10). **Complete**

PROGRESS TOWARD MILESTONES

Last quarter a Si/graphene-composite electrode was constructed using two-dimensional graphene sheets and porous silicon. The self-assembled structure consisted of alternating layers of graphene nanosheets and micron-sized porous Si. There was no binder used in this free-standing electrode. The reversible capacity of the Si was *ca*. 2500 mAh/g in the first 20 cycles. The effects of binders on the cycle stability of Si-based anodes were also investigated during this quarter.

A special binder P that can stabilize the Si anode was developed. Micron-sized porous Si particles coated with CVD carbon were made into anodes using binder P instead of PVDF. The capacity fading rate was reasonably small and the reversible capacity stayed at *ca*.1000 mAh/g at the high current density of 400 mA/g (Fig. 1). When cycled in a limited voltage range (0.17 to 0.9 V), the capacity fade per cycle was only 0.7% after the first two formation cycles. Therefore, using binder P as a substitute for PVDF is an alternative, simple, and economic means of improving the cycling performance of Si-based anodes.

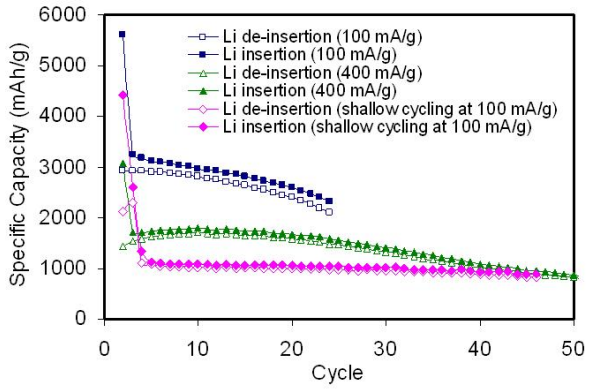


Figure 1. Silicon cycling stability at high current density (400 mA/g) and shallow cycling condition (0.17-0.9 V).

Technical goals proposed for FY 2010 were completed. The Si/graphene electrode was prepared and demonstrated a high capacity of 2343 mAh/g based on Si (or 781 mAh/g based on the anode weight) after 30 cycles. The CVD-coated, porous Si demonstrated a reversible capacity of more than 1600 mAh/g based on Si (or 960 mAh/g based on anode weight) after 30 cycles. In FY11, novel synthetic methods will be developed to synthesize Si nanoparticles. These nanoparticles (<100 nm) will be used to replace the micron-sized porous Si. Carbon additives and binder P will be used to reduce the irreversible capacity loss and improve the electrochemical performance of the whole electrode. New types of carbon materials will be developed as three-dimensional conducting scaffolding for Si nanoparticles.

Publication: "Stabilization of Silicon Anode for Li-Ion Batteries." J. Xiao, W. Xu, D. Wang, D. Choi, W. Wang, X. Li, G.L. Graff, J. Liu, and J-G. Zhang, *J. Electrochem. Soc.*, **157**, A1047- (2010).

Collaborations: I.A. Aksay, Princeton University and Vorbeck Inc., provided the graphene for this work. Prashant N. Kumta, University of Pittsburgh, helped to deposit Si nanoparticles in novel carbon materials using the CVD-deposition method.

BATT TASK 3
ELECTROLYTES
TASK STATUS REPORT

TASK 3.1 - PI, INSTITUTION: Nitash Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Development of Polymer Electrolytes for Advanced Lithium Batteries

SYSTEMS: Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Needs improved energy density and safety.

OBJECTIVES: Synthesize PS-PEO-PS triblock copolymers with varying molecular weights and compositions to obtain electrolytes with high ionic conductivity and shear modulus. Electrochemically characterize PS-PEO-PS/LiTFSI electrolytes against Li-metal anodes in symmetric cells, with planar $LiCoO_2$ cathodes, and with sulfur cathodes. Use block copolymers to create mesoporous battery separators for conventional liquid electrolytes.

GENERAL APPROACH: Synthesize and characterize dry PS-PEO-PS polymer electrolytes. Continue to characterize salt/polymer mixtures by AC impedance spectroscopy, and make DC measurements with Li | polymer electrolyte | Li cells to obtain diffusion coefficients and Li transference numbers. Collaborate with members of the BATT Program to test stability of the electrolyte against electrodes (Li metal, planar $LiCoO_2$, and sulfur). Also, synthesize and characterize porous PS-PE polymer separators by synthesizing a block copolymer, blending with a homopolymer, and washing out the homopolymer to yield a porous block copolymer.

STATUS OCT. 1, 2009: Synthesis of new PS-PEO-PS and PS-PE block copolymers underway. Equipment for solution casting membranes designed and operational. Development of a procedure for testing batteries with porous PS-PE with conventional liquid electrolyte begun.

EXPECTED STATUS SEP. 30, 2010: Stability testing of the PS-PEO-PS samples against planar electrodes will be ongoing. The effect of morphology on the transference number and diffusion coefficient (obtained from DC testing) will be measured. The solubility of Li polysulfides in PS-PEO-PS will be measured. The conductivity of conventional liquid electrolyte in porous PS-PE separators will be measured. Cycling porous PS-PE with liquid electrolyte in full batteries will be started.

RELEVANT USABC GOALS: EV applications goals are a specific energy of 200 Wh/kg and a specific pulse power of 400 W/kg.

MILESTONES:
(a) Synthesize and characterize the morphology of new PS-PEO-PS samples. (Mar. 10). **Complete**
(b) Cast PS-PEO-PS membranes, measure ionic conductivity, transference numbers, and diffusion coefficients. Demonstrate battery cycling with PS-PEO-PS, Li anodes, and planar cathodes. (Sep. 10) **Complete**
(c) Synthesize porous PS-PE and measure ionic conductivity of polymer/liquid electrolyte mixture. (Sep. 10) **Complete**
(d) Measure solubility of lithium-sulfur compounds in PS-PEO block copolymers. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Milestone (b) was completed, although the results suggest that further studies are warranted. Free-standing PS-PEO-PS membranes were used to demonstrate battery cycling with planar $LiCoO_2$ cathodes and Li-metal anodes. Theoretical capacities were obtained at low current densities but significant capacity fade was observed upon cycling and higher current densities. Equipment was recently installed to facilitate the assembly of cells with Li-metal anodes. This led to considerable improvement in the data obtained from cells with a porous $LiFePO_4$ cathode. The new equipment will be used to make the second generation of cells with planar $LiCoO_2$ cathodes.

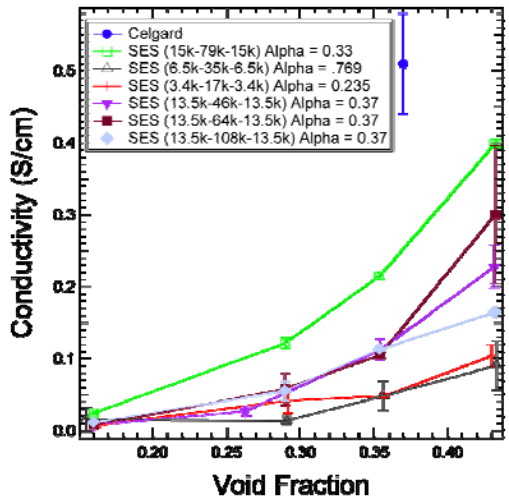


Figure 1. Conductivity of porous SES with 1M $LiPF_6$ in EC/DEC *vs*. void fraction. Data sets as a function of molecular weight and Alpha are shown.

The work with regard to milestone (c) was completed. PS-PE-PS block polymers (SES) were synthesized with a porous structure by addition of a homopolymer polystyrene with a higher molecular weight than used previously. The ionic conductivity of a series of porous SES with 1M $LiPF_6$ in EC/DEC was measured, see Fig. 1. The different porous SES block polymers are described by molecular weight and Alpha, where Alpha is the ratio of the molecular weight of the homopolymer to the molecular weight of the styrene block in the SES. This ratio should be indicative of important aspects of the transport properties of the resultant separators. The conductivity of the separators increased with increasing molecular weight of the styrene block at relatively constant Alpha values. No work was performed on cycling porous SES separators in full cells. Better understanding of the effect of Alpha on the separator's properties is sought before deciding on an optimal composition to synthesize.

Milestone (d) was completed on schedule. The solubility of Li_2S_x ($1 \leq x \leq 8$) compounds was studied using XRD, SAXS, and DSC in a series of symmetric SEO polymers at r = 0.03, 0.085, 0.125 where r = $[Li^+]/[EO]$. XRD indicated precipitation of lithium sulfide at low values of x (x = 1, 2) and showed complete solubility of the longer chain polysulfides at all concentrations tested. This result is consistent with trends seen in the literature for other systems, including organic solvents, organic electrolytes, and homopolymers. SAXS in Fig. 2 showed that, although short-chain polysulfides precipitated, the morphology of the samples remained unchanged, suggesting that the precipitated salt was confined within the domains of the microstructure. SAXS also showed that soluble lithium sulfides could induce ordering in the SEO block copolymers. The DSC data showed that as the value of x increased, the crystallinity of the PEO block decreased. The loss of crystallinity is an indirect measure of the solubility, and, thus, as x increased, the solubility increased.

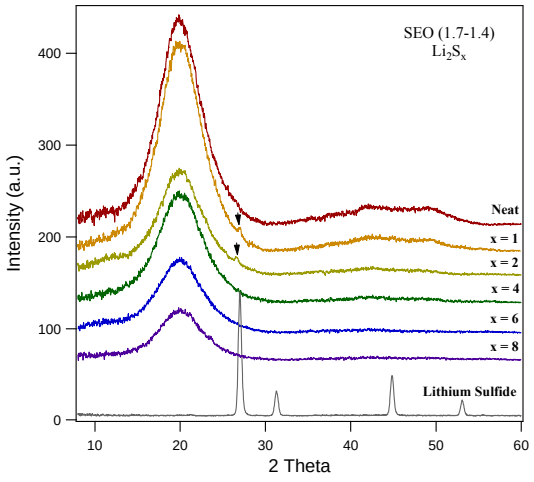


Figure 2. Mixtures of SEO(1.7-1.4) with Li_2S_x showing precipitation of Li_2S for x=1, 2. All samples at r = 0.085 except x=8 at r = 0.125.

TASK 3.2 - PI, INSTITUTION: John Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Poor cycle and calendar life, low power and energy densities, particularly at low temperatures (-30^{o}C) and high cost.

OBJECTIVES: 1) Determine the role of electrolyte structure upon the intrinsic electrochemical kinetics and how it contributes to the interfacial impedance. 2) Determine how bulk and electrode reactions of electrolytes contribute to impedance growth and lead to battery failure. 3) Evaluate the use of very high rate polymer electrodes and redox active binders

GENERAL APPROACH: A physical-organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the various processes that may affect the performance of the battery. This involves model compounds as well as new synthesis of materials to test hypotheses which may explain battery behavior.

STATUS OCT 1. 2009: More detailed studies on the nature of the source of interfacial impedance will be complete. For anodes some of the effects of the SEI layer have been distinguished from that of the intrinsic electrochemical rates of reaction. Similar studies have attempted to determine whether there are cathode films formed and whether they degrade performance. Variation of the nature of the electrolyte provides information on the fundamental electrode kinetics.

EXPECTED STATUS SEP. 30, 2010: It is expected that the behavior of single ion conductor polyelectrolytes with different cathodes will be sufficiently explored to confirm the benefits of such electrolyte systems with regard to electrode thicknesses and hence increased energy density. The effect of particle size on this behavior will be evaluated as will the possible effect of the interfacial impedance in the composite electrodes. Similar studies on silicon and tin alloy anodes will be carried out to evaluate the benefits of polyelectrolytes on large volume-change electrodes.

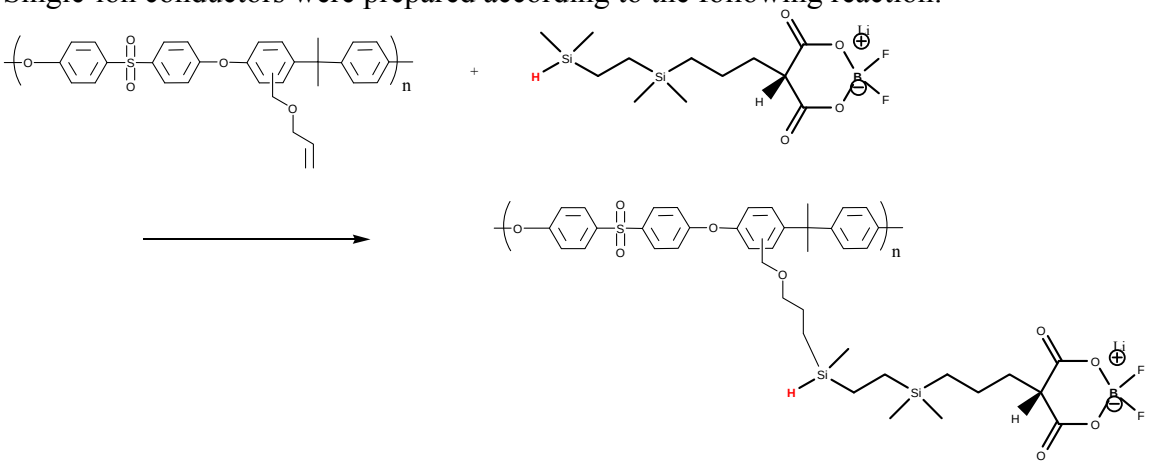
RELEVANT USABC GOALS: EV- 200 Wh/kg, 400 W/kg for a 30 sec. discharge

MILESTONES:
(a) Demonstrate whether single-ion conductor polyelectrolytes (gel and dry polymer) prevent concentration polarization in composite cathodes and facilitate thicker electrodes. (Jun. 10) **On going, delayed to Nov. 10**
(b) Determine whether single-ion conductor polyelectrolytes (gels and dry polymers) are beneficial for large volume-expansion anodes. (Sep. 10) **On going, delayed to Jan. 11**

PROGRESS TOWARD MILESTONES

Use of single-ion conductor polyelectrolytes (gel and dry polymer) to provide high energy composite electrodes due to increased thickness - Milestone (a) mostly completed, remainder due November 2010; and Milestone (b) partly completed, expected completion January 2011.

Single-ion conductors were prepared according to the following reaction:



Another material was also successfully prepared using fluoroalkylsulfonylimides (TFSI) and does not contain the ether group in the side chain and, hence, should be stable to at least 5V. The difluoromalonoborate (DFMB) material shown above was cast as a film and imbibed with γ-butyrolactone(GBL) as the solvent. The conductivity of this gel electrolyte membrane was measured to be 3.85×10^{-5} S/cm (–4.4 on the log scale) at room temperature. The interfacial impedance and cycling behavior are shown in the figures below.

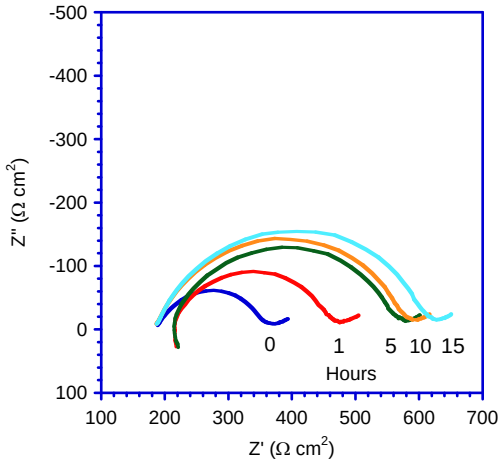


Figure 1. Impedance over time for single-ion conductor at Li Metal; as assembled and 1, 5, 10 and 15 hours after assembly.

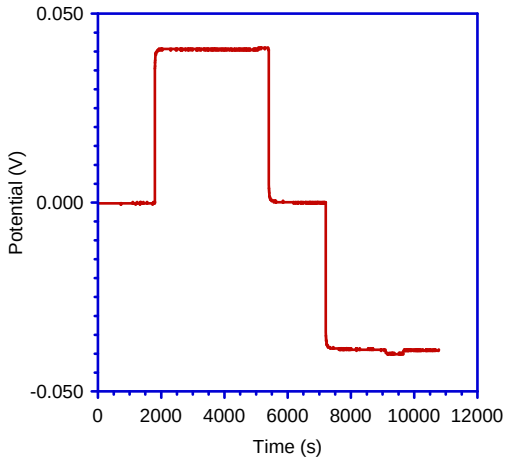


Figure 2. First charge/discharge cycle at Li metal for single-ion membrane.

The reduction of the interfacial impedance from 1000's of ohms to hundreds is very encouraging and the cycling shown in Fig. 2 indicates the lack of salt diffusion and hence the lack of concentration polarization. Experiments with composite electrodes are under way to achieve the milestones.

Task 3.3 - PI, INSTITUTION: Grant Smith and Oleg Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes – Modeling: Molecular Modeling of Electrodes, SEI, Electrolytes, and Electrolyte/Electrode Interfaces

SYSTEMS: Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Poor low-temperature operation, transport through SEI layer and cycle life, high interfacial resistance.

OBJECTIVES: Prediction and investigation of structure and formation of the SEI using reactive MD simulations. Prediction and understanding of properties of novel electrolytes. Prediction and understanding of charge transfer resistance to graphite and $LiFePO_4$ electrodes. Improved understanding of electric double layer structure, capacitance and transport as a function of electrode potential and temperature for mixed carbonate electrolytes.

GENERAL APPROACH: Utilize developed force fields and simulation methods to simulate novel electrolytes. Utilize recently developed electroactive interface model to study electric double layer properties and charge transfer processes at the cathode/electrolyte and anode/electrolyte interfaces. Utilize reactive force field (ReaxFF) methods to study SEI formation at Li-metal and graphite/electrolyte interfaces.

STATUS OCT 1. 2009: All codes and models except parallel ReaxFF simulation code are in place. All systems to be studied in investigations of SEI structure, anode charge transfer resistance, cathode charge transfer resistance, electric double layer structure, capacitance and transport, and novel electrolytes, except those requiring parallel ReaxFF simulation code, have been determined and implemented.

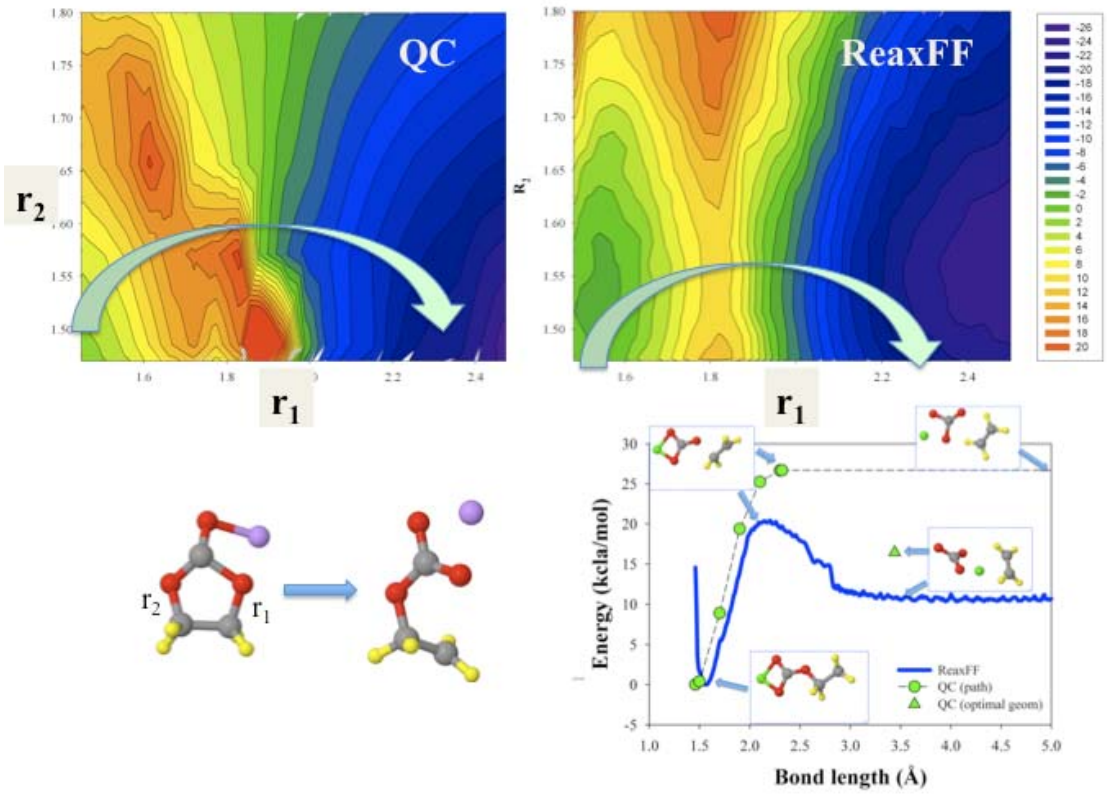
EXPECTED STATUS SEP. 30, 2010: Parallel ReaxFF simulation code will be fully implemented. All simulations associated with the prediction of SEI structure on graphite anodes and of charge transfer resistance at the graphite/electrolyte and $LiFePO_4$ electrolyte interface will be completed. Model studies of the double-layer structure, capacitance and charge transport for metallic electrodes with mixed carbonate electrolytes as a function of electrode potential will be completed. Simulation studies of novel electrolytes in collaboration with Henderson (NCSU) will be completed.

RELEVANT USABC GOALS: *10-s discharge power:* 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:
(a) Complete investigation of electric double layer structure for mixed carbonate electrolytes as a function of electrode potential. (Mar. 10) **Complete**
(b) Complete investigation of charge transfer resistance for graphite and $LiFePO_4$ electrodes. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

In collaboration with Adri van Duin (Penn State) the force field for reactive simulations (ReaxFF) was re-parameterized to allow better agreement with quantum chemistry data on reaction paths of EC radical/Li^+ complexes. The new version of the force field captures most of the characteristics of key reaction pathways between radicals. Specifically, as illustrated in the Figure below, the new force field captured a complex pathway for cyclic-EC radical opening, which required deformation of two C-O bonds in EC, as well as the pathway for breaking ethylene away from the linear-EC radical.



Molecular dynamics simulations of electrolyte solutions with various compositions of cyclic- and linear-EC radicals identified several possible pathways for radical recombinations and formation of oligomeric alkyl carbonates. Simulations with the new force field revealed that the linear-EC radical has a much higher probability to find and attack the carbonate group of another EC radical (cyclic or linear) than to find another linear-EC radical in such orientation that would allow radical recombination and the formation of dilithium butylene dicarbonate. These results are consistent with the latest experimental data that questions the presence of dilithium butylene dicarbonate in EC-based SEIs. The ability to react with the carbonate group of another radical is likely to be the pathway for formation of dilithium ethylene dicarbonate, which is believed to be the primary component of the outer SEI layer. However, we also found that reaction of linear-EC radical with the carbonate group of another EC radical does not always lead to radical elimination and that the newly formed compound can react with a few more radicals before radical termination. This indicated that longer alkyl carbonate oligomers can be present in the SEI.

TASK 3.4 - PI, INSTITUTION: Khalil Amine and Larry Curtiss, Argonne National Laboratory

TASK TITLE - PROJECT: Electrolytes - Advanced Electrolyte and Electrolyte Additives

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High voltage, high power: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiMn_2O_4$

BARRIERS: Cycle/calendar life, abuse tolerance

OBJECTIVES: Develop an Advanced Quantum Model to predict functional additives that form stable SEI on carbon anodes and cathodes. Expand model to predict how additives interact with the surface of anode and cathode during initial charging. Synthesize suitable additives predicted by model, characterize and perform extensive cycle and calendar life tests.

GENERAL APPROACH: Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings. Use density functional studies of graphite surface reactions to determine mechanisms for protective film formation from additives.

STATUS OCT 1, 2009: We have the initial development of state-of-the-art quantum chemical models (REF1, REF2) to assist in the screening of potential additive candidates by predicting their oxidation and reduction potentials, and to verify that they would be operable over the desired potential window.

EXPECTED STATUS SEP. 30, 2010: We will have developed a first version of the quantum model and will initiate the fine tuning of the model to predict the redox-potential and ionization energies of potential additives.

RELEVANT USABC GOALS: 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:
(a) Screen over 100 candidate materials for reduction potentials. (Aug. 09) - delayed because work started in late April. (Apr. 10) **Complete**
(b) Initiate investigation of reactions on electrode surface of decomposition products. (Apr. 10) **Complete**
(c) Develop and optimize a quantum model that helps identify new functional electrolyte additives. (Sep. 10) **Complete**
(d) Develop quantum chemical models for polymerization pathways of electrolyte additives that can be used for screening. (Sep 10) **Complete**
(e) Develop a model to predict the potential of redox shuttle to improve safety. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

A quantum chemical approach for identifying new functional electrolytes for formation of a protective SEI on the anode was completed. This approach is based on quantum chemical models for calculating reduction potentials, decomposition pathways, and polymerization reactions. These quantum chemical models are based on density functional theory with a continuum model applied for inclusion of solvation effects. The models include calculations of structures, electron affinities, and transition states. A quantum chemical model was also developed for assessing the likelihood that redox shuttles would be stable based on the calculation of oxidation potentials and thermochemical data for possible decomposition pathways. These theoretical approaches will be used in future work on screening of additives for SEI formation and redox shuttles. Work on all milestones in FY10 was completed.

Anionic polymerization reactions are well known and can be important in the formation of a passivating SEI layer on the anode. Approaches based on density functional theory have been developed to screen the reductive decomposition of additives to form anion radicals that can attack other species to form polymer-like components in the SEI. In Fig. 1, an anion radical of an additive, formed by reduction, is shown attacking a neutral additive molecule. The reaction energy was characterized using density functional theory; gas-phase and solution-free energies, and energy barriers (not shown) were calculated to assess kinetics.

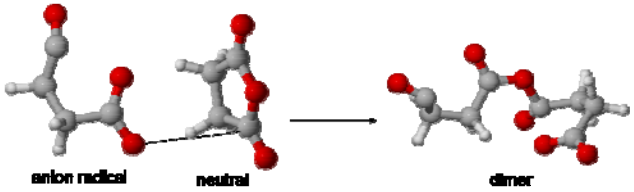


Figure 1. Dimerization reaction of an additive molecule.

Redox shuttles for overcharge protection need to be stable and not decompose under high potentials. A quantum chemical model for assessment of potential candidates with high oxidation potentials was developed based on density functional theory. In this approach, structures of the neutral molecule and the oxidized cation radical are optimized. Then gas-phase and solution-free energies are calculated and used to determine the oxidation potential, providing an idea of how easy it is to remove an electron from the molecule and, hence, its likelihood to decompose. The model can also be used to determine how changes in ligands affect the oxidation potentials. The model uses accurate quantum chemical calculations of free energies using large basis sets to determine whether decomposition is likely to occur. Figure 2 shows an example of two possible decomposition pathways for a redox shuttle on which this approach was tested. The results provided a better understanding of this class of redox shuttles.

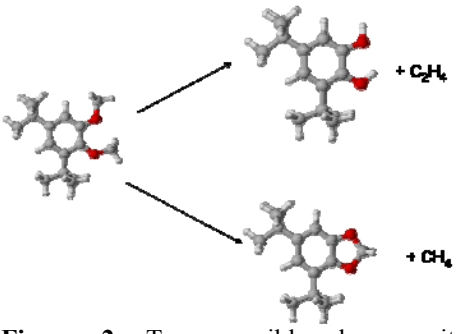


Figure 2. Two possible decomposition pathways for an oxidized redox shuttle.

TASK 3.5 - PI, INSTITUTION: Brett Lucht, University of Rhode Island

TASK TITLE - PROJECT: Electrolytes - Development of Electrolytes for Lithium-ion Batteries

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High-voltage, high-power: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiMn_2O_4$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Cell performance, life, cost: Calendar life: 40°C, 15 yrs; Survival Temp Range: -46 - 52°C

OBJECTIVES: Develop novel electrolytes or electrolyte/additive combinations that will facilitate a more stable SEI on the anode. Develop additives that allow for formation of protective coatings on the cathode, *i.e.*, a cathode SEI, and enhances electrochemical stability above 4.5 V.

GENERAL APPROACH: Investigate properties of $LiPF_4C_2O_4$/carbonate electrolytes in small Li-ion cells with multiple cell chemistries. Develop commercially viable low-cost synthetic method for production of $LiPF_4(C_2O_4)$ and produce high purity $LiPF_4(C_2O_4)$ for additional testing. Develop novel additives and additive combinations to improve the performance of $LiPF_6$ electrolytes. Investigate cathode film forming additives for high voltage (>4.5 V) cathode materials. Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation.

STATUS OCT. 1, 2009: Contract placed April 1, 2009. We have investigated a new salt for Li-ion batteries, $LiPF_4(C_2O_4)$ in graphite/$LiNiCoO_2$ coin cells. $LiPF_4(C_2O_4)$ electrolytes have comparable performance to $LiPF_6$ electrolytes. We have prepared 100 g of $LiPF_4(C_2O_4)$ for additional testing. Some of this material has been provided to commercial partners and some will be provided to BATT collaborators (Battaglia). We have also shown $LiPF_6$ electrolytes containing combinations of additives, thermal stabilizing, and anode film forming, can provide cells with superior high temperature resilience to cells containing a single additive.

EXPECTED STATUS SEP. 30, 2010: We will have developed cathode film forming additives that improve the cycling performance of graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells cycled to high voltage (4.9 V *vs.* Li). We will have expand our investigation of the novel salt $LiPF_4(C_2O_4)$ by testing in coin cells under accelerated aging conditions, graphite/$LiMn_2O_4$ electrodes, and electrolytes containing PC.

RELEVANT USABC GOALS: 10 s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); Calendar life: 40°C, 15 yrs; Survival Temp Range: -46 – 52°C; Cold cranking power at -30°C; Cycle life.

MILESTONES:
(a) Develop cathode film forming additives for high voltage (>4.5 V *vs*. Li) cathode materials. (Mar. 10) **Complete**
(b) Investigate cell performance upon accelerated aging of graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells with $LiPF_4(C_2O_4)$ electrolytes compared to $LiPF_6$ electrolytes. (Mar. 10) **Complete**
(c) Investigate cell performance of $LiPF_4(C_2O_4)$ compared to $LiPF_6$ in small cells with new chemistries graphite/$LiMn_2O_4$ and $LiNi_xCo_{1-2x}Mn_xO_2$ cells with PC electrolytes. (Sep. 10) **Complete**
(d) Develop commercially viable synthesis for $LiPF_4(C_2O_4)$. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

With regards to milestone (a), results were reported as completed in our Q2 report. Various additives were incorporated into $Li/Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ cells, which improved the performance at high voltage, as described in both our Q1 and Q2 reports.

With regards to milestone (b), results were also reported as completed in our Q1 and Q2 reports. The results suggested similar improved resilience under accelerated aging with both cell chemistries.

With regards to milestone (c), preliminary cycling was conducted with $LiPF_4(C_2O_4)$/PC electrolyte. The cycling of the cells with the $LiPF_4(C_2O_4)$/PC electrolyte was comparable to the standard $LiPF_6$ electrolyte and much better than the $LiPF_6$/PC electrolyte, as described in the Q2 report. Surface analysis suggested that the performance differences were related to an inhibition of graphite exfoliation in the presence of $LiPF_4(C_2O_4)$. XPS analysis suggested that an effective SEI was formed on the anode covering the PVDF binder (C1s, 290.3 and 285.7 eV) when either standard electrolyte ($LiPF_6$ in EC/EMC) or $LiPF_4(C_2O_4)$/PC electrolyte are used. $LiPF_6$/PC electrolyte does not cover the PVDF, suggesting poor SEI formation (Fig. 1). Initial cycling was also conducted with graphite/$LiMn_2O_4$ and graphite/$LiFePO_4$ coin cells. The $LiPF_4(C_2O_4)$ electrolyte cycled well in both systems. The discharge capacity of graphite/$LiFePO_4$ cells was very similar for $LiPF_4(C_2O_4)$ and $LiPF_6$ electrolytes. Interestingly, in the graphite/$LiFePO_4$ cells, there was a very small difference in the initial irreversible capacity for $LiPF_4(C_2O_4)$ compared to $LiPF_6$. Subsequent surface analysis of the electrodes indicated that the electrode surfaces were very similar. However, the discharge capacity was slightly lower for graphite/$LiMn_2O_4$ cells containing $LiPF_4(C_2O_4)$ instead of $LiPF_6$.

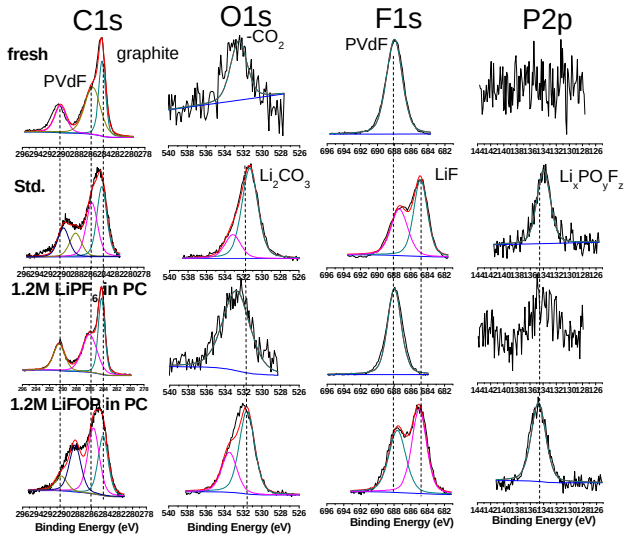


Figure 1. XPS surface analysis of graphite anodes cycled with PC based and standard electrolytes.

With regards to milestone (d), a superior method for the preparation of $LiPF_4(C_2O_4)$ was developed, which provided significantly higher yields. Initial analysis suggested that this synthetic method has commercial viability. Work is currently going on with industrial partners to scale up the process.

Collaborations this Quarter: B. Ravdel (Yardney)**,** D. Abraham (ANL), M. Smart (NASA-JPL), W. Li (S. China Univ. Tech.), V. Battaglia (LBNL) and M. Payne (Novolyte).

Publications this quarter: (1) M. Xu, L. Zhou, L. Xing, W. Li, B.L. Lucht *Electrochim. Acta*, **2010**, *55*, 6743-6748. **(2)** L. Yang, B. Ravdel, and B.L. Lucht, *Electrochem.& Solid State Lett.*, **2010**, *13*, A95-A97.

TASK 3.6 - PI, INSTITUTION: Daniel Scherson and John Protasiewicz, Case Western Reserve University

TASK TITLE - PROJECT: Electrolytes - Bifunctional Electrolytes for Lithium-ion Batteries

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Abuse tolerance

OBJECTIVES: (a) Design, synthesize, and characterize physical, electrochemical, and interfacial characteristics of functionalized single-component, Li-salt anions containing phosphorous moieties known to impart materials with flame retardant properties (Flame Retardant Ions or FRIONS). (b) Develop bifunctional electrolytes to allow species to support charge transport through the electrolyte and to provide flame retardant properties and/or overcharge protection, and thereby improve device safety.

GENERAL APPROACH: Design, synthesis, and evaluation of multifunctional materials for battery applications. Build database of fundamental knowledge on this chemistry. Impart electrolyte bifunctionality by incorporating covalently linked groups to anions known to display high conductivity and stability with flame retardant and/or overcharge protection characteristics.

STATUS OCT. 1, 2009: Design, assemble, and partially test the electrochemical cell for *in situ* acquisition of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) data. Acquire all necessary chemicals to initiate synthesis and characterization of phosphorous-containing analogues of LiBOB (LiBOP) class of FRIONS. Refine syntheses to afford large quantities of these materials in high purity form.

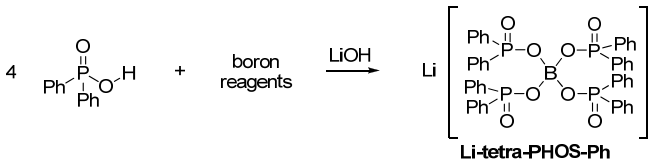
EXPECTED STATUS SEP. 30, 2010: Full implementation and initial data collection employing *in situ* ATR-FTIR measurements aimed at monitoring *in situ* composition of the electrolyte and surface films following cycling of a single model anode and single model in conventional carbonate-based electrolytes and materials synthesized and characterized under this program. Completion of synthesis, purification and characterization of first generation of LiBOP-type FRIONs in amounts sufficient for electrochemical testing. Synthesis and preliminary testing of several members of the CBPO (cyclic borate phosphine oxides) type of FRIONs.

RELEVANT USABC GOALS: No fire or rapid disassembly of cells during abuse conditions.

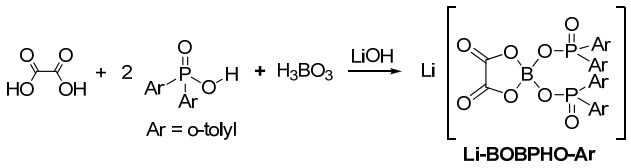
MILESTONES:
(a) Identify *in situ* the nature of solution phase products and composition of passive films on single model anodes and cathodes of relevance to the USABC objectives involving well established electrolytes using ATR-FTIR techniques. (Mar. 10) **Delayed, due Sep. 10**
(b) Prepare and fully characterize three new LiBOP type FRIONs. (Mar. 10) **Delayed, due Sep. 10**
(c) Extend the same techniques to examine newly developed bifunctional electrolytes. (Jun. 10 & Sep. 10) **Delayed to Mar. 11**
(d) Prepare and characterize new FRIONS based on properties of LiBOP-type FRIONs found during previous trimester. (Jun. 10) **Delayed to Mar. 11**
(e) Synthesize and characterize completely new class of FRIONs (CBPOs). First example of CBPO will be achieved, and initial evaluation will be accomplished. (Jun. 10) **Delayed to Mar. 11**
(f) Characterize and test three (or more) members of CBPO class of FRIONs. (Sep. 10) **Delayed to Mar. 11**

PROGRESS TOWARD MILESTONES

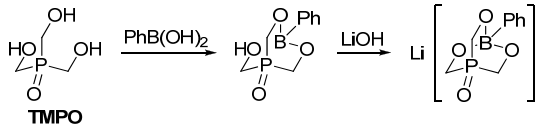
a. Synthesis of FRIONS – In the last quarter, our collaborators at Novolyte Technologies demonstrated that adding LiBOBPHO-Ph FRION to a button cell had no detrimental effects on cell performance. Encouraged by these results, a second generation of phosphinic acid-based FRIONS was synthesized. Initially, the synthesis of Li-tetra-PHOS-Ph was targeted by the reaction of 4 equivalents of diphenylphosphinic acid with boric acid and lithium hydroxide at various temperatures, solvents, and conditions to little avail (Scheme 1). Additionally, boron trichloride, boron tribromide, boron trioxide, and trimethylborate were used as starting materials but the Li-tetra-PHOS-Ph was not formed under these conditions either. Furthermore, lithium borohydride was unsuccessfully reacted with four equivalents of diphenylphosphinic acid in various solvents and temperatures. Attempts were made to synthesize H-tetra-PHOS-Ph using a similar methodology, however none of this material was ever observed. In hopes to generate a more reactive phosphorus source, the above reactions were carried out using diphenyl (tri-methylsilyl)phosphine, synthesized from hexamethyldisilazane and diphenylphosphinic acid, but these reactions also did not lead to the targeted species. Further progress in substituting the LiBOBPHO-Ph series of FRIONs was achieved by replacing the phenyl rings of the diphenylphosphinic acid moiety with di-o-tolylphosphinic acid (Scheme 2). Our hopes are that this substitution will increase the solubility of the FRION, leading to an easier isolation process. Progress was also made in another class of FRIONS (Scheme 3). Previously, the reaction of TMPO with phenylboronic acid was met with limited success. However, switching to a more polar reaction solvent, the subsequent borate ester was formed, exclusively, as determined by NMR. Unfortunately, closure of the system has not yet been attained.



Scheme 1



Scheme 2



Scheme 3

b. Spectroscopic Studies: Attenuated Total Reflection FTIR - A photograph of the cell for conducting *in situ* ATR-FTIR measurements designed and constructed in our laboratory is shown in the figure. The cell was made out of propylene and incorporates unique features that help mitigate problems associated with impurities. The upper knob allows for a Ni rod electrode isolated from the atmosphere to move along the vertical axis, z, whereas the left knob makes it possible to translate a stainless steel rod along an axis normal to z which houses at its end a piece of Li foil. Once the cell is filled with electrolyte, the Ni rod is lifted and the Li foil placed directly beneath and at a very small distance from the flat end of the Ni electrode. Application of a current between the Li and Ni electrodes allows for a film of pure Li to be deposited on the flat surface of the Ni rod. Once the deposition is completed, the Li foil is retrieved and the Ni rod is lowered and pressed directly against the diamond window in the base for spectroscopic examination.

Publications this Quarter: Shaffer, A.R., Deligonul, N., Scherson, D.A., and Protasiewicz. J.D. A Hybrid Lithium Oxalate-Phosphinate Salt. *Inorg. Chem.* Accepted.

TASK 3.7 - PI, INSTITUTION: Wesley Henderson, North Carolina State University

TASK TITLE - PROJECT: Electrolytes - Inexpensive, Nonfluorinated Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Low cost cell materials, abuse tolerance, low temperature performance

OBJECTIVES: Develop new anions as replacements for PF_6^- or as additives for electrolytes

GENERAL APPROACH: Synthesize and fully characterize two classes of nonfluorinated anions: 1) chelated and non-chelated organoborate anions (related to bis(oxalate) borate (BOB^-)), and 2) Hückel-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both Li salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as $LiPF_6$ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion.

STATUS OCT. 1, 2009: A new lithium organoborate salt containing 2-hydroxyisobutyric acid has been synthesized/purified and the crystal structure of the monohydrate of the salt has been determined. The thermal phase behavior of binary mixtures of LiBOB with EC, PC and GVL and $LiBF_4$ with EC, GVL, DMC and DEC has been determined to provide a baseline for solvent interactions for newly prepared salts relative to currently used salts.

EXPECTED STATUS SEP. 30, 2010: New salts based upon organoborate and Hückel-type anions will have been prepared and some of these will be scaled up for extensive characterization. Ionic liquids will also have been prepared from these anions and characterized. The phase behavior and properties of solvent-LiBOB, -LiODFB, and -$LiBF_4$ mixtures will have been determined for comparison with the new salts and to aid in understanding the widely varying solubility noted for these salts.

RELEVANT USABC GOALS: Available energy: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); cycle life: 5000 cycles (10 mile) and 3000 cycles (40 mile); calendar life: 15 years (at 35°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:
(a) Scale up synthesis of organoborate salt based upon 2-hydroxyisobutyric acid. (Dec. 09) **Incomplete (change in research direction - no longer relevant)**
(b) Scale up synthesis of lithium dicyanotriazolate (LiDCTA). (Dec. 09) **Complete**
(c) Explore/characterize new anions (organoborate and Hückel). (Sep. 10) **On going, due Apr. 11**
(d) Electrolyte property characterization and phase diagram preparation. (Sep. 10) **On going, due Apr. 11**

PROGRESS TOWARD MILESTONES

Organoborate Salts:
The preparation of phase diagrams were underway for aprotic solvent/lithium difluoro(oxalato)borate (LiODFB) mixtures with ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and tetramethylene sulfone (sulfolane or TMS). The data to date indicates that the EC and PC mixtures are unable to form crystalline solvates, whereas DMC, DEC, and TMS do form crystalline solvates in dilute mixtures. The structure of the $(TMS)_2$:LiODFB was determined (Fig. 1). This is a contact ion pair (CIP) dimer structure in which the Li^+ cations are coordinated by one anion through a single oxylate carbonyl oxygen and three other oxygens (one each from three solvent molecules). The dimer structure is formed by two (of the four) solvent molecules coordinating two different Li^+ cations each. This structure demonstrates the multiple modes of Li^+ cation coordination available for this solvent. The synthesis of additional difluoro(ligand)borate anions is underway.

Partially Fluorinated Cyanocarbanions: Work continued on the characterization of the phase behavior and solvates formed in solvent/lithium dicyanotriazolate (LiDCTA) mixtures. The preparation of partially fluorinated cyanocarbanions and dianions with extensive resonance across the anion structures has been ongoing with recent work devoted to purifying the salts.

Several new lithium organoborate salts were prepared, but these exhibited poor solubility in aprotic solvents. Although Hückel-type anions such as LiDCTA have significantly improved solubility (relative to the organoborates), the ions were highly aggregated in solution. Ionic liquids, which were prepared and characterized with the $DCTA^-$ anion, however, had favorable properties including a low T_m and viscosity. The focus for the project thus shifted to partially fluorinated organoborate and cyanocarbanions anions to improve the Li salt solubility and decrease ion association. LiODFB synthesis was scaled-up, with the material produced at high purity. Numerous phase diagrams of solvent/LiBOB, /LiODFB and /$LiBF_4$ mixtures were prepared to examine the variability in solvation and ionic association due to the differences in their anionic structure.

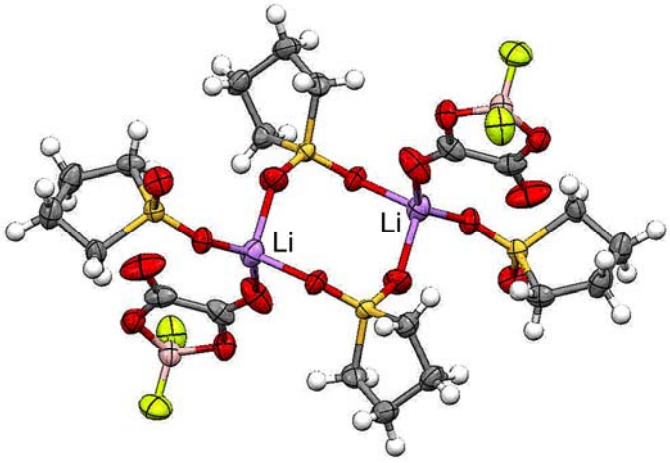


Figure 1. Ion coordination in the crystal structure of the $(TMS)_2$:LiODFB solvate (Li: purple, B: tan, O: red, F: green, S: gold).

TASK 3.8 - PI, INSTITUTION: C. Austen Angell, Arizona State University

TASK TITLE - PROJECT: Electrolytes – Sulfones with Additives as Electrolytes

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Needs increased oxidation resistance and decreased viscosity, and improved safety. Improved safety will follow with successful fluorination methods.

OBJECTIVES: To devise new electrolyte solvent chemistries that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection.

GENERAL APPROACH: The approach is twofold: 1) to design new solvent molecules that retain the high oxidation resistance already demonstrated for noncyclic sulfones while maintaining the solubility of $LiPF_6$ and lowering the liquid viscosity, and 2) to ascertain which cosolvents will act with ethylmethyl sulfone (or fluoropropylmethyl sulfone) to produce the same effect. (It has already been demonstrated that at least some cosolvents of lower oxidation resistance are somehow protected from oxidation when mixed with fluoropropylmethylsulfone or related high voltage resistance sulfone solvents.)

STATUS OCT. 1, 2009: This is a new project initiated May 1, 2010.

EXPECTED STATUS SEP. 30, 2010: Commercially available methyl sulfonyl fluoride, the properties of which, as solvent, were not known at the start of this project will have been evaluated. It is found to have limits as a single solvent (because of poor solubility of $LiPF_6$), but to be interesting as a cosolvent with EMS from the point of view of conductivity (factor of 3 more conductive than with pure EMS as solvent). However the oxidative stability is not good. Likewise for methane sulfonyl chloride, which had previously been studied as a single solvent and found to have a wide "voltage operating window". The latter case has been instructive to demonstrate limits on synergism of EMS with cosolvents. Where initial experience suggested all co-solvents might experience enhanced stability deriving from the presence of the sulfone, this case proves that it cannot be assumed to be general.

Attempts will have been made to fluorinate one or more of the ring methylene groups on the familiar wide-"window" electrolyte solvent tetramethylene sulfone (sulfolane), for which a substantially reduced viscosity is predicted.

RELEVANT USABC GOALS: EV: 1000 cycles (80% DoD); 10 year life. An electrolyte with electrochemical window of 5.2 volts and conductivity of 20 mS/cm.

MILESTONES: This is a new project in FY 2010.
(a) Evaluate 50% cosolvent systems and determine useful limits. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONE

In the early stages of this program, studies were made on (a) a commercially available but previously untested sulfone (methanesulfonylfluoride (MSF)), (b) a known but commercially unavailable and untested sulfone (trifluoromethylmethyl sulfone), and (c) a previously unknown *fluorinated* version of the known and tested cyclic sulfone, sulfolane ($(CH_2)_4SO_2$. The latter two were successfully synthesized in the ASU lab. In both cases, Li-salt solutions were prepared and characterized. Results and their significance are summarized below.

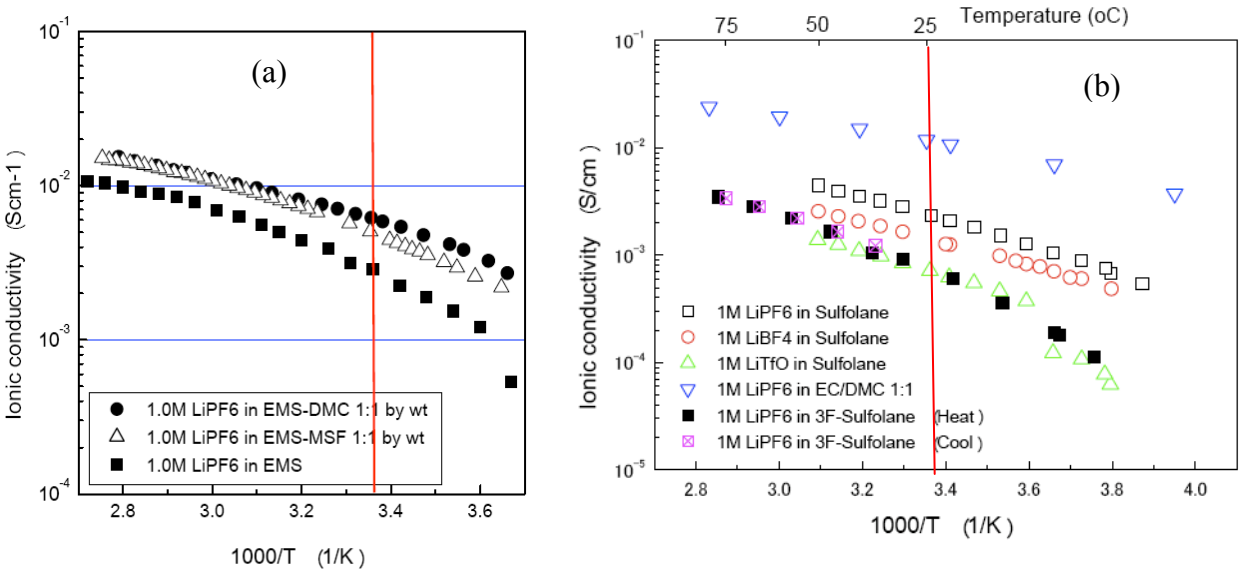


Figure 1. Ionic conductivities of 1 molar Li-salt solutions in (a) the wide electrochemical window solvent ethylmethylsulfone, and two 50:50 (by wt) mixtures with (i) dimethylcarbonate and (ii) methane sulfonyl fluoride, (b) the known "wide window" solvent sulfolane and its new monofluorinated derivative 3Fsulfolane. Data for $LiPF_6$ in standard EC-DMC solution are shown for comparison. The new solvent is evidently less dissociating (lower dielectric constant) and will need EC cosolvent for good performance.

1:1 EMS:MSF conductivity is almost as good as is 1:1 EMS + DMC, (which is within a factor of 2 of the conductivity of the standard carbonate electrolyte (~20mS/cm)), but MSF is toxic and undesirable. The new fluorinated sulfolane has an excellent (5.6V) electrochemical "window" (Fig. 2) but is not as dissociating as sulfolane. A Walden plot, Fig. 3, is used to demonstrate the dissociating power of sulfolane; the fluorinated solvent will be characterized the same way.

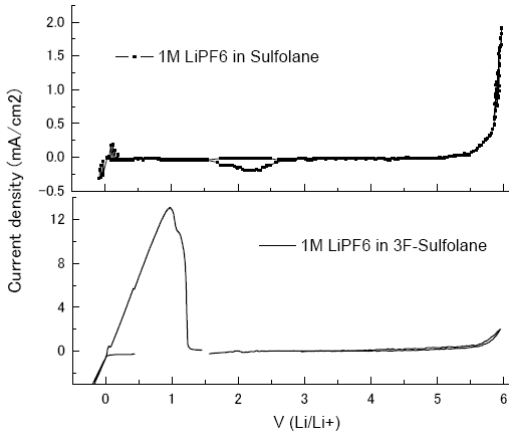


Figure 2. Electrochemical window for 3F sulfolane.

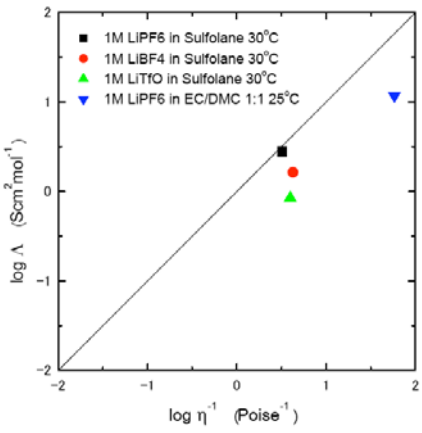


Figure 3. Walden plot for sulfolane solutions.

Collaborations this Quarter: Oleg Borodin, University of Utah, collaborated on the effects of fluorination on the properties of fluorinated cyclic sulfones.

BATT TASK 4
CATHODES

TASK STATUS REPORT

Task 4.1 - PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Cathode Materials

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High voltage, high power: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiMn_2O_4$

BARRIERS: Low energy, cost, and abuse tolerance limitations of Li-ion batteries

OBJECTIVE: To develop low-cost, high-energy and high-power Mn-oxide-based cathodes.

GENERAL APPROACH: We will continue to exploit the concept of using integrated 'layered-layered' $xLi_2M'O_3 \bullet (1-x)LiMO_2$ structures to stabilize high-capacity (>200 mAh/g) electrodes in which M′ is predominantly Mn and M is Mn, Ni and Co. In FY 2010, we will focus our efforts on 1) protective coatings to stabilize the electrodes at high potentials, 2) an autogenic reaction process to synthesize and carbon-coat cathode materials in a single step, using $LiFePO_4$ as a prototype system for our initial studies, and 3) atomic scale simulations to model and characterize the interface and atomic arrangement in coated $LiMn_2O_4$ electrodes.

STATUS OCT 1. 2009: The rate capability of high capacity $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Mn, Ni, Co) electrodes for Li-ion batteries was significantly enhanced by stabilizing the electrode surface with a lithium-nickel-phosphate coating. Reversible capacities in excess of 200 mAh/g were obtained at a C/1 or slower rate. Theoretical studies of the solubility and surface structure of $LiMn_2O_4$ in an acidic medium were completed.

EXPECTED STATUS SEP. 30, 2010: Progress will have been made in enhancing the surface stability of composite $xLi_2M'O_3 \bullet (1-x)LiMO_2$ electrode structures at high potentials. Improvements in electrochemical properties, notably rate and cycle life, can be expected. A new process for coating cathode particles with carbon will have been evaluated. Theoretical simulations of coated electrode surfaces will have been conducted.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:
(a) Evaluate a single-step, autogenic process for synthesizing carbon-coated cathodes. (Apr. 10) **Complete**
(b) Engineer and evaluate the electrochemical effects of protective coatings on composite electrode structures with a high Mn content (Sep. 10) **Complete**
(c) Model coatings and interfacial phenomena at the surface of $LiMn_2O_4$ electrodes (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Collaborators: S.-H. Kang (co-PI), Donghan Kim
Milestone (b) addressed: Engineer and evaluate protective coatings on composite electrodes.

Accomplishments

In terms of R&D efforts and the results thereof, all three milestones were successfully accomplished. The work resulted in 3 publications, 1 patent application, and 10 presentations.

A new project on structurally-integrated cathode materials, such as 'layered-layered' xLi_2MnO_3•$(1-x)LiMO_2$ systems (M = Mn, Ni, Co) was initiated to study the effect of Ni and Co coatings on the electrochemical properties of xLi_2MnO_3•$(1-x)LiCoO_2$ and xLi_2MnO_3•$(1-x)LiNiO_2$ electrode particles, respectively, as well as Mn coatings on $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ ('NCA') electrode particles. The project is being conducted to support the characterization of surface structures at Argonne's Advanced Photon Source in a parallel, EERE-funded effort. For the initial studies, $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ (or $0.5Li_2MnO_3$•$0.5LiCoO_2$) was prepared by mixing Li_2CO_3 and coprecipitated $(Mn_{0.5}Co_{0.5})CO_3$ and calcined at 850°C for 12 hr in air. Thereafter, the $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ product was treated with an acidic solution (pH<2) containing lithium acetate, nickel nitrate, and ammonium dihydrogen phosphate (Li:Ni:P=1:1:1). The treated powder was heated to 550°C for 6 hr in air. Lithium half cells were cycled at 15 mA/g between 4.6 and 2.0 V (that included a constant voltage charge at 4.6 V for 3 h). Electrochemical data are provided in Figs. 1 and 2.

A significant improvement in the first cycle efficiency (CE1) was obtained from the treated cathode (Fig. 1a). Corresponding voltage profiles of the 1st and 20th cycles of these two cells are shown in Figs. 1b and 1c, respectively. The data highlight the superior electrochemical properties of the surface treated electrode, in terms of both capacity retention and lower polarization during charge and discharge, particularly after cycling. The rate capability of the treated electrode was determined to be superior to the untreated electrode (Figs. 2b and 2a, respectively), using current rates of A: 15 mA/g; B: 30 mA/g; C: 75 mA/g; D: 150 mA/g; E: 300 mA/g; and F: 750 mA/g.

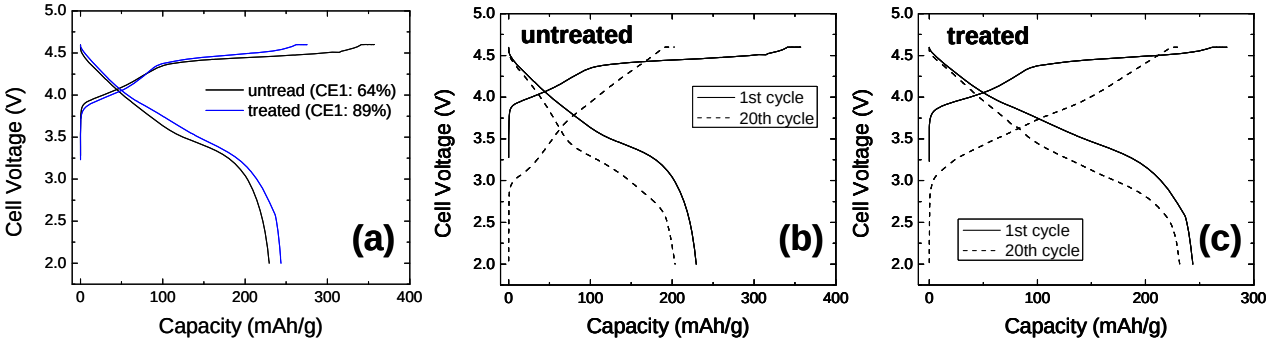


Figure 1. Electrochemical data of Li/$Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ half cells with untreated and treated cathodes.

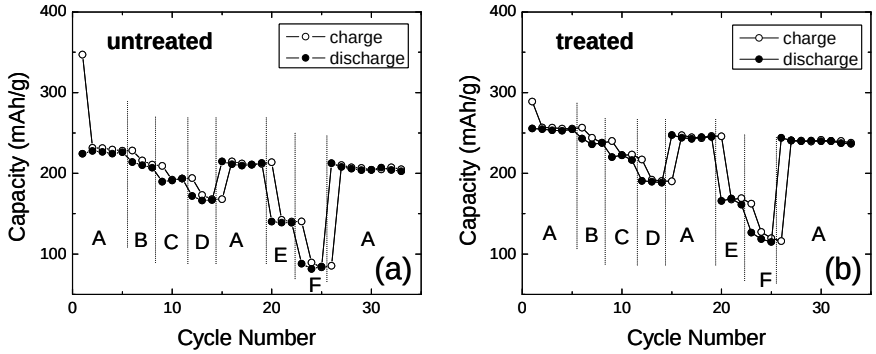


Figure 2. Rate capability of Li/$Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ half cells with untreated and treated cathodes.

TASK 4.2 - PI, INSTITUTION: M. Stanley Whittingham, Binghamton University

TASK TITLE - PROJECT: Cathodes - Materials: Novel Cathodes

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Lower-cost, higher power, higher-capacity and abuse-tolerant safer cathodes

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials.

GENERAL APPROACH: Our cathode approach is to place emphasis on low cost oxides and phosphates, both pure and modified with other transition metals, using a range of practical synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT 1. 2009: We have determined that layered metal dioxides can be structurally stabilized with around 3% Ni in the Li layer, that their electronic conductivity and cycling can be significantly enhanced by the addition of additional metals, and that in the 1:1 lithium/metal compounds the cobalt content can be reduced to 10%. We have completed an electrochemical and thermodynamic evaluation of $LiFePO_4$ as a base-case, low-cost cathode, shown that substitution is possible on the lithium, iron, and phosphorus sites. We have shown that nanostructured material containing around 5% isovalent substitution has the highest capacity with as little as 6 wt% carbon.
• $LiFePO_4$: > 120 Ah/kg for 100 cycles at 1 mA/cm^2.
• Layered $Li_xCo_zNi_yMn_{1-y-z}O_2$: 160 Ah/kg and 150 Ah/kg for 60 cycles at 1 and 2 mA/cm^2 respectively.

EXPECTED STATUS SEP. 30, 2010: For low-cost Li-ion cells, we expect to identify the changes in (a) electrochemistry, (b) rate capability (PHEV), and (c) $LiMnO_2$ structures as a function of substitution level as in $Li_xMn_{1-y-z}Ni_yCo_zO_2$, so as to determine the optimum minimum cobalt substitution level. We will have extended our studies beyond olivine-structured lithium metal phosphate and evaluated some manganese containing iron phosphates (non-olivine), and explored some higher capacity next generation cathodes.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, and lower cost batteries.

MILESTONES:
(a) Determine the optimum composition of $LiNi_yMn_yCo_{1-2y}O_2$ for PHEV applications. (Mar. 10) **Go on cobalt contents of ≤ 0.2**
(b) Evaluate phosphate structures with varying morphologies and dopants, containing Fe and/or Mn, and compare with optimum $LiFePO_4$. (Sep. 10) **1st phase complete**
(c) Identify materials that can undergo more than one electron per redox center. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Layered Transition Metal Oxides. A range of transition metal oxides of formula $LiNi_yMn_yCo_{1-2y}O_2$ were formed to determine the optimum composition for both energy density and power density. The theoretical capacity was determined by measuring the open circuit voltages on both Li removal and Li insertion. The material with y = 0.4 showed as good behavior as any other composition. For PHEV applications, a continuous rate capability of 1C to 2C is needed. The rate capability of the layered materials is perceived to be less than that of olivine and spinel, particularly when Li rich. The inherent rate capability of the 40% Ni composition material was sought. This composition is believed to be an optimum based on cost, safety, and capacity considerations. The results are shown in Fig. 1.

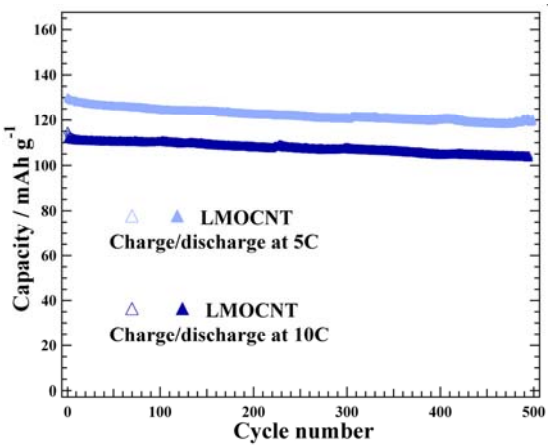


Figure 1. Capacity at 5C and 10C cycling rate for $LiNi_{0.4}Mn_{0.4}Co_{0.22}O_2$, on a carbon nanotube mesh grid.

These results were obtained in collaboration with C. Ban and A. Dillon of NREL - the material was synthesized and characterized at Binghamton and evaluated electrochemically at NREL. The oxide was spread on a carbon nanotube mesh with no binder and no additional carbon. The results in Fig. 1 clearly show that the layered materials can provide significant capacity at high rates when the electrode is configured optimally. The capacity at a 5C rate well exceeds 120 mAh/g. This excellent behavior is consistent with the high Li diffusion coefficients measured, as shown in Fig. 2.

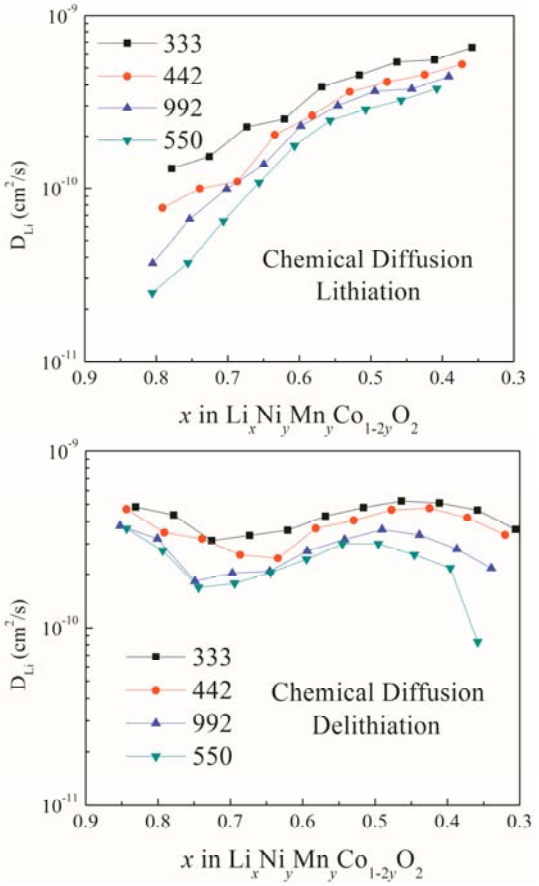


Figure 2. The lithium in- and out-diffusion coefficients in $LiNi_yMn_yCo_{1-2y}O_2$.

Publications and Presentations

(1) This work was presented at the IMLB meeting in Montreal in June 2010.

Further plans to meet or exceed milestones: None

A collaboration with NREL (A. Dillon and C. Ban) to determine the rate capability of the layered oxides, specifically $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$, was initiated. Some of the results are provided in this report.

Reason for changes from original milestones: No changes

TASK 4.3 - PI, INSTITUTION: Marca Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-ion Batteries

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Cost, power and/or energy density, cycle life

OBJECTIVES: To develop low-cost benign cathode materials having electrochemical characteristics (*e.g.,* cycle life, energy and power densities) consistent with the USABC goals.

GENERAL APPROACH: Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties. Some work is directed toward surveying new materials with potential for increased energy density.

STATUS OCT 1. 2009: A no-go decision has been made on $LiMnPO_4$ due to its unsuitability for vehicular applications. Future work is restricted to tying up loose ends for a publication. Extensive characterization of the $Li[Ni_{0.4}Co_{0.2-y}Al_y\ Mn_{0.4}]O_2$ this year indicates that the observed improved rate capability can be attributed to structural effects of the Al substitution (the Li slab spacing is increased). Iron substitution worsens the electrochemical behavior, and Ti substitution is limited to very low levels but appears to improve rate capability similar to Al.

EXPECTED STATUS SEP. 30, 2010: Further characterization of the $Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ system will be carried out with BATT members (Persson, Whittingham, Grey) using modeling, NMR, magnetic measurements, and spectroscopic methods to obtain a deeper understanding of the structural details that affect rate capability. Synthesis and characterization of $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ will be carried out. A spray pyrolysis method is under development to prepare carbon-containing nanocomposites. This has been used to make $LiMnPO_4$/C materials because the synthetic parameters are well known. Once optimized, we will transition to the synthesis of other promising polyanionic compounds such as $LiMnBO_3$, $Li_2(Mn, Fe)SiO_4$, and $LiVPO_4F$.

RELEVANT USABC GOALS: High power, low cost (HEV). High energy, low cost, cycle life (EV, PHEV).

MILESTONES:
(a) Synthesize and electrochemically characterize $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ series. (Jun. 10) **Complete**
(b) Develop spray pyrolysis method for synthesis of cathode materials, including polyanionic compounds. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

$Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$ was characterized with XANES and associated techniques (with E. Cairns, UC Berkeley, and A. Deb, U. Michigan) and a paper was published. Evaluation of this material in full cells will be carried out in FY11 (with V. Battaglia, LBNL). A series of $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ compounds were synthesized and electrochemically characterized. Synchrotron studies were being carried out on selected materials using both *in situ* and *ex situ* techniques (with J. Cabana, LBNL, and A. Mehta, SSRL). This work will continue into FY11. High performance $LiFePO_4$/C composites and $LiCoPO_4$/C composites were prepared by spray pyrolysis (with T. Richardson, LBNL). Preparation of $LiMnPO_4$/C composites has met with less success and will require modification of the set-up. Spray pyrolysis will be extended to other cathode materials of interest (oxides, other polyanionic compounds) in FY11.

4.3a. *In situ* diffraction studies carried out at SSRL showed that the c-axis parameter underwent less change during oxidation in $Li_{1-x}[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O_2$ than in $Li_{1-x}[Ni_{0.45}Co_{0.1}Mn_{0.45}]O_2$ (Fig. 1). The smaller volume decrease in the former may explain its better cycling behavior. EXAFS data on $Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$ undergoing cell charge and discharge also showed that M-O and M-M bondlength changes were highly reversible.

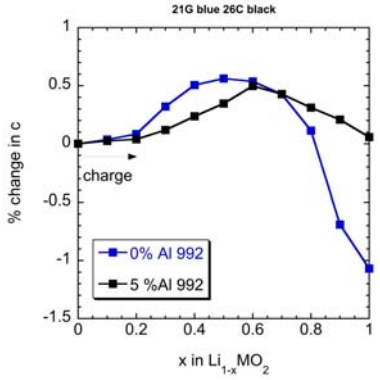


Figure 1. Variation of c-parameter with state-of-charge for $Li_{1-x}[Ni_{0.45}Co_{0.1}Mn_{0.45}]O_2$ and $Li_{1-x}[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O_2$ cathodes.

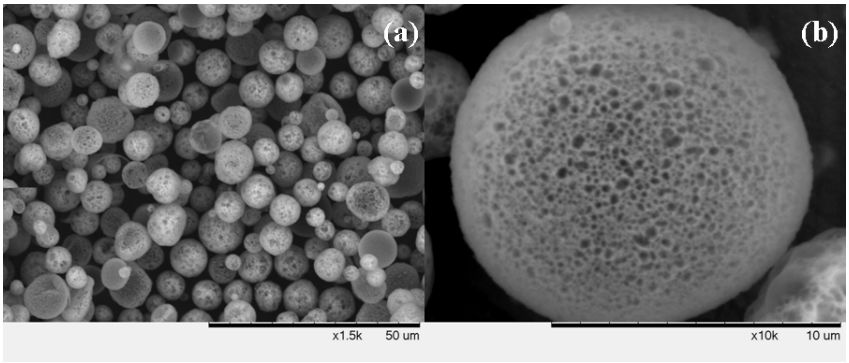


Figure 2: Nanoporous $LiFePO_4$/C spheres produced by spray pyrolysis at a) 1.5 and b) 10x magnification.

4.3b. Spray pyrolysis of $LiFePO_4$/C and $LiCoPO_4$/C composites resulted in the production of nanoporous, solid LFP- and hollow LCP-spheres (Fig. 2). Both materials showed excellent electrochemical performance. Several papers are in preparation.

Publications and Presentations

1) "Structural and Electrochemical Investigation of $Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2$ Cathode Material" C. Rumble, T.E. Conry, Marca Doeff, Elton J. Cairns, James E. Penner-Hahn, and Aniruddha Deb, *J. Electrochem. Soc.* **157**, A1317 (2010).

2) "Combustion Synthesis of Nanoparticulate $LiMg_xMn_{1-x}PO_4$ (x=0, 0.1, 0.2) Carbon Composites" Marca M. Doeff, Jiajun Chen, Thomas E. Conry, Ruigang Wang, James Wilcox, and Albert Aumentado, *J. Mater. Res.*, **25**, 1460 (2010).

3) "Advanced Li-ion Battery Cathode Materials for Vehicle Technologies" Marca M. Doeff, American Chemical Society, Electrochemistry and Battery Applications symposium, August 2010, Boston, MA, Paper 355.

4) "The Effect of Al-Substitution in $LiNi_{0.45}Co_{0.1-x}Al_xMn_{0.45}O_2$ Layered Oxide Cathode Materials" T. Conry, J. Cabana, and M Doeff, 218th meeting of the Electrochemical Society, October 2010, Las Vegas Nevada, Abstract 1000.

TASK 4.4 - PI, INSTITUTION: Arumugam Manthiram, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – High-Performance Cathode Materials

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Cost, cycle life, safety, power density, and energy density

OBJECTIVES: To develop (i) low-cost spinel manganese oxide compositions that can offer excellent capacity retention, high energy and power, and good storage characteristics at elevated temperatures and (ii) low-cost cathodes based on polyanions that can offer a combination of high energy and power with excellent thermal stability and safety.

GENERAL APPROACH: Our approach is to continue to develop a firm scientific understanding of the factors that control/influence the electrochemical performances of the cathodes and utilize the knowledge gained to design and develop high performance spinel and polyanion-containing cathode compositions. In this regard, (i) cationic and anionic substitutions and surface modifications of spinel oxide cathodes and (ii) novel cathode compositions consisting of polyanions are being pursued. Particularly, self segregation of certain substituted cations to the surface during the synthesis process that can suppress Mn dissolution in 4 V spinel cathodes or control the SEI layer formation in high voltage (~5 V) spinel cathodes is investigated. Conventional ceramic synthesis and innovative synthesis approaches such as microwave-assisted solvothermal and template-assisted methods that can offer controlled nanomorphologies, advanced chemical and structural characterizations, and electrochemical evaluation with lithium and carbon anodes are being pursued. Based on the characterization data gathered, a fundamental understanding of the structure-composition-property-performance relationships is developed.

STATUS OCT 1. 2009: Development of stabilized 4 V and 5 V spinel compositions through chemical substitutions and surface modifications, optimization and evaluation of spinel-layered composite cathodes, novel synthesis and evaluation of cathodes based on polyanions including nano olivines, and an investigation of their structure-property-performance relationships.

EXPECTED STATUS SEP. 30, 2010: Development of stabilized 4 V and 5 V spinel cathode compositions through self surface segregation and chemical surface modifications, microwave-assisted solvothermal and template-assisted syntheses of cathodes based on polyanions with nanorod and nanowire morphologies, and an investigation of their structure-composition-property-performance relationships.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, 10-year life, <20% capacity fade over a 10-year period

MILESTONES:
(a) Characterize surface modified stabilized spinel cathodes. (Mar. 10) **Complete**
(b) Develop polyanion-containing cathodes with controlled nanomorphologies. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Previously it was shown that the olivine $LiMPO_4$ (M = Mn, Fe, Co, and Ni) cathodes can be obtained by microwave-assisted solvothermal (MW-ST) and microwave-assisted hydrothermal (MW-HT) methods at temperatures under 300°C within a short reaction time of 5 to 15 minutes. Following this, the MW-ST method was extended to synthesize the silicate cathode materials, such as Li_2FeSiO_4 and Li_2MnSiO_4. These materials offer the possibility of reversibly extracting/inserting two Li ions per formula unit with a theoretical capacity of *ca*. 330 mAh/g. In addition, the low cost of Fe, Mn, and Si, as well as the operation of the $M^{2+/4+}$ couples with covalently-bonded SiO_4 groups offering high thermal stability and safety, make them attractive candidates for large-scale applications. However, only limited literature is available on this class of materials due to the difficulty in synthesizing phase-pure Li_2MSiO_4, and they suffer from poor electronic conductivity like the olivine phosphates. Developing new synthesis methods to obtain nanostructured Li_2MSiO_4 with an electronically conductive coating may improve their electrochemical performance.

Accordingly, in this quarter, the focus was on the synthesis of nanostructured Li_2MSiO_4 by the MW-ST process at 300°C for 20 min, followed by heating at 650°C for 6 h in an Ar atmosphere. The result was well-crystalline samples with a carbon coating. XRD confirmed the formation of phase-pure Li_2MSiO_4 after heat treatment. SEM and TEM images showed agglomerated nanoparticles with an average particle size of *ca*. 20 nm. The smaller particle size along with the carbon coating was beneficial toward improving Li-ion diffusion kinetics and electronic conductivity, respectively, and thereby the rate capability. Figures 1(a) and (b) show the charge-discharge profiles at C/20 of Li_2FeSiO_4/C and Li_2MnSiO_4/C at room temperature and at 55°C. At room temperature, Li_2FeSiO_4 and Li_2MnSiO_4 delivered a first discharge capacity of 148 and 210 mAh/g, respectively. Moreover, at 55°C, the discharge capacities of Li_2FeSiO_4 and Li_2MnSiO_4 increased significantly to, respectively, 204 and 250 mAh/g, demonstrating the ability to extract/insert more Li at high temperatures. The increase in capacity and Li extraction at high temperatures was attributed to enhanced kinetics.

As seen in Fig. 1(c), Li_2FeSiO_4/C exhibited a stable cycle life with 100% capacity retention at both room temperature and 55°C, demonstrating its good reversibility and structural integrity during cycling. In contrast, Li_2MnSiO_4/C exhibited drastic capacity fade, especially at 55°C - after 20 cycles it retained only 50% of its initial capacity at room temperature and 15% at 55°C. This poor capacity retention of Li_2MnSiO_4/C is believed due to the presence of Mn^{3+} ions, which could lead to a dynamic Jahn-Teller distortion and Mn dissolution, as is the case with $LiMn_2O_4$-spinel cathodes. In addition, while Li_2FeSiO_4 exhibited high rate performance and good thermal stability, Li_2MnSiO_4 showed poor rate performance and low thermal stability.

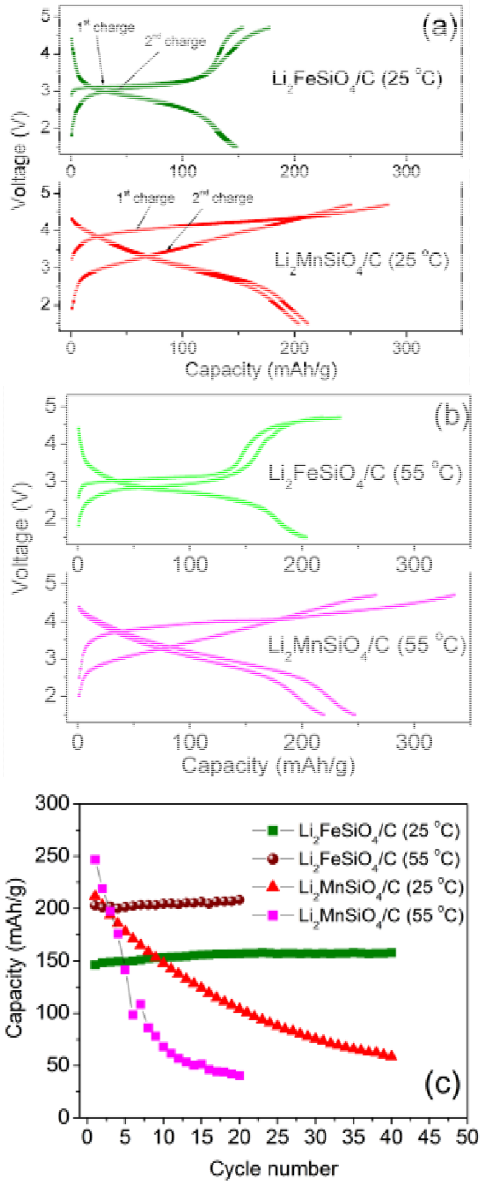


Figure 1. Charge-discharge profiles and cycle life of Li_2MSiO_4/C.

TASK 4.5 - PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE – PROJECT: Cathodes – Development of High Energy Cathode Materials

SYSTEMS: High voltage, high power: Graphite/1 M $LiPF_6$ in EC:DEC 1:2/$LiMn_2O_4$
Low-voltage, high stability: Graphite/1 M $LiPF_6$ in EC:DEC 1:2/$LiFePO_4$

BARRIERS: Low energy density, cost, cycle life

OBJECTIVES: To develop high energy, low-cost, and environmentally-benign cathode materials.

GENERAL APPROACH: Our approach is to develop phosphate-based high voltage cathode materials (including $LiMnPO_4$, Li_2CoPO_4F, and $Li_3V_2(PO_4)_3$) with good capacity and discharge rate. Several cost effective synthesis routes, including single-step, solid-state reaction in molten hydrocarbon and precipitation methods, will be adopted in this work. Environmentally-benign organic cathodes that exhibit two or more electrons per redox center will also be evaluated as PHEV and EVs compatible cathode materials. The structural stability, morphology variation, and thermal stability of these materials will be investigated to improve their electrochemical performances (including their capacity and cyclability).

STATUS OCT. 1, 2009: Project initiated Jan. 1, 2010. Preferred growth of $LiMnPO_4$ nanoplates without agglomeration is prepared by a single-step, solid-state reaction with molten hydrocarbon. High reversible capacity (~130 mAh/g) was achieved at C/25 rate with a stable cycling ability. A novel cathode material, Li_2CoPO_4F, has been synthesized and characterized. Up to 1 mole of Li^+ ions are reversible in Li_2CoPO_4F within 2.0-5.5 V, probably due to the strong bonding of F with the second Li.

EXPECTED STATUS SEP. 30, 2010: The synthesis condition of high-performance $LiMnPO_4$ will be optimized. The feasibility of using $LiMnPO_4$ to substitute the existing commercial cathode materials will also be evaluated. The nonstoichiometry study of Li_xMnPO_4 ($0.5 \leq x \leq 1.2$) will be investigated to find the clues of the Li^+ diffusion mechanism in the $LiMnPO_4$ system. Anthraquinone-based polymer cathode materials will be synthesized and the operation voltage of this high capacity material will be tuned by adjusting the functional groups to further improve its energy density.

RELEVANT USABC GOALS: 145 Wh/l (=11.6 kWh/80L) of usable energy, improved abuse tolerance and less than 20% capacity fade over a 10-year period.

MILESTONES:
(a) Investigation of Li_2CoPO_4F with two reversible Li^+ ions. (Mar. 10) **Complete**
(b) Synthesis and characterization of $LiMnPO_4$ with high energy and rate capability. (Sep. 10) **On going, due date Apr. 11**
(c) Influence of lithium content on the long term cycling of $LiMnPO_4$. (Sep. 10) **Complete**
(d) Synthesis and characterization of poly(anthraquinonyl sulfide) (PAQS) with redox process based on the quinonyl group.(Sep. 10) **On going, due date Sep. 11**

PROGRESS TOWARD MILESTONES

The high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ was investigated at PNNL. The following progress was made during the last quarter:

1. A simple, cost-effective synthesis was developed that included milling and heating steps. The approach lends itself to scale-up.
2. The spinel was prepared with a particle size of about 2 μm, which further aggregated into larger secondary particles that improved its packing density.
3. Different electrolytes and additives were investigated to improve its 1st-cycle efficiency.

The synthesis route for $LiNi_{0.5}Mn_{1.5}O_4$ spinel started with the mixing of Li_2CO_3, $MnCO_3$, and NiO was followed by heating to high temperatures. Figure 1 shows the XRD pattern of the as-prepared $LiNi_{0.5}Mn_{1.5}O_4$ spinels. A very small amount of Li_xNi_yO was detected while all of the other peaks were indexed to the spinel structure with *Fd3m* space group, suggesting a disordered, non-stoichiometric $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$. Figure 2 displays the morphologies of the as-prepared $LiNi_{0.5}Mn_{1.5}O_4$ spinels. The average particle size of the primary particles was around 2 μm (see TEM inset in Fig. 2). These uniformly distributed particles further aggregated into secondary particles (also seen in Fig. 2). This morphology had higher packing density than that of nano-particles, which should prove beneficial in practical applications.

The voltage profiles of micron-sized $LiNi_{0.5}Mn_{1.5}O_4$ were plotted in Fig. 3. In a conventional electrolyte consisting of $LiPF_6$ in EC/EMC, the initial discharge capacity approached 130 mAh/g with a 1st-cycle coulombic efficiency of 73%. A small plateau at around 4.0 V was observed, which is consistent with a residual amount of Mn^{3+}, as was revealed in the XRD patterns of Fig. 1. When EMS/DMS was used as the solvent, the 1st-cycle efficiency was improved to 80% with no loss of discharge capacity.

The long-term cycling of as-prepared $LiNi_{0.5}Mn_{1.5}O_4$ is underway and will be compared with that of doped spinels from future efforts. Electrolyte/additive optimization will also continue in an attempt to further improve the first cycle coulombic efficiency.

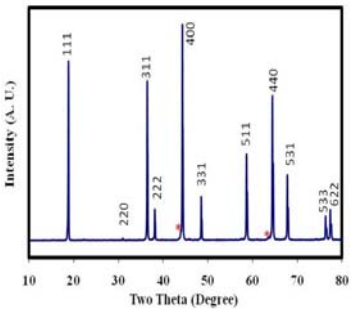


Figure1. XRD patterns of $LiNi_{0.5}Mn_{1.5}O_4$

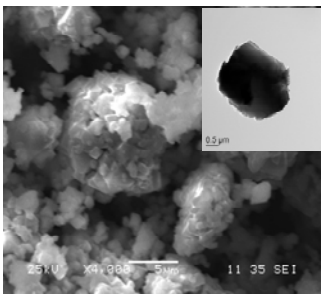


Figure 2. Morphologies of as-prepared $LiNi_{0.5}Mn_{1.5}O_4$

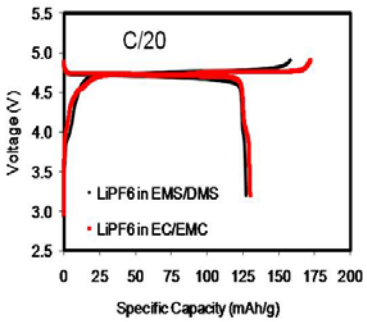


Figure 3. Voltage profiles of $LiNi_{0.5}Mn_{1.5}O_4$ in different electrolytes.

Publication:

1. D. Wang, J. Xiao, W. Xu, Z. Nie, C. Wang, G. Graff and J-G. Zhang, *J. Power Sources*.2010.10.21.

Collaborations: The new cathode, Li_2CoPO_4F, developed at PNNL was delivered to ARL for further evaluation with their high-voltage electrolyte.

BATT TASK 5
DIAGNOSTICS
TASK STATUS REPORT

TASK 5.1 - PI, INSTITUTION: Robert Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Interfacial Processes: Diagnostics

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIER: Low energy (related to cost), poor Li battery calendar/cycle lifetimes.

OBJECTIVES: (i) Establish direct correlations between electrochemical performance of high-energy Li-ion cathodes, and surface chemistry, morphology, topology and interfacial phenomena, (ii) improve the capacity and cycle life limitations of alloy anodes.

GENERAL APPROACH: Our approach is to (i) adopt and apply an electrochemical cell of the Devanathan-Stachurski type to study the kinetics of Li alloying and diffusion in intermetallic anodes, and possible correlations with the formation and long-term stability of the SEI layer, (ii) apply *in situ* and *ex situ* Raman and FTIR spectroscopy/microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, electron microscopy (SEM, HRTEM), and standard electrochemical techniques to detect and characterize surface processes in intermetallic anodes, and high-energy cathodes.

STATUS OCT. 1, 2009: We gained insight into the mechanism of detrimental surface phenomena on thin-film intermetallic anodes and evaluated their impact on the electrode long-term electrochemical behavior. Comprehensive fundamental study of the early stages of SEI layer formation on Sn and Si electrodes revealed formation of an unstable surface film layer. *In situ* spectroscopic ellipsometry in conjunction with AFM and FTIR/Raman surface analysis were applied to detect and monitor surface phenomena at the intermetallic anodes and showed that some reaction products diffuse into the electrolyte. *In situ* and *ex situ* Raman and FTIR spectroscopy were used to determine surface and bulk composition in high-voltage (>4.3V) composite cathodes.

EXPECTED STATUS SEP. 30, 2010: We expect to define the physico-chemical parameters of the intermetallic alloys and their interfacial properties that determine long-term electrochemical performance of intermetallic anodes in Li-ion systems. These include: (i) charge and mass transfer parameters for Sn, Si, and Al alloys, (ii) basic electrocatalytic properties of alloy materials, (iii) the effect of material structure, crystallinity, morphology and composition. *In situ* and *ex situ* Raman and FTIR spectroscopy will be used to determine and characterize surface and bulk processes in composite $LiMnPO_4$ cathodes.

RELEVANT USABC GOALS: *Cycle life*: 5000 (deep) and 300,000 (shallow) cycles. *Available energy*: 96 Wh/kg. *Calendar life*: 15 years.

MILESTONES:
(a) Characterize surface phenomena in $LiMnPO_4$ composite cathodes. (Jul. 10) **Complete**
(b) Identify the structural and surface changes of Al, Si and Sn-containing anodes during cycling working collaboratively with the BATT SEI Group. (Sep. 10) **Complete.**

PROGRESS TOWARD MILESTONES

During the 4th quarter of FY10, the mechanism of interfacial processes at intermetallic anodes was investigated. *In situ* spectroscopic ellipsometry and AFM measurements were applied to gain better understanding of the electrolyte decomposition processes and SEI layer (re)formation upon cycling of tin anodes.

Preliminary *in situ* AFM and ellipsometry measurements of a Sn-foil electrode in EC-based electrolytes at potentials > 0.7 V, *i.e.*, above the potential of Sn–Li alloying, revealed the formation of an unstable SEI. The anomalously high irreversible cathodic process observed in the cyclic voltammograms of polycrystalline Sn (reduction peak at 1.3V on Fig. 1) was attributed to catalytic decomposition of the electrolyte.

To better understand the basic electrocatalytic properties of Sn in organic carbonate/$LiPF_6$ electrolytes, interfacial phenomena of the surface at selected crystalline orientations were investigated using single crystal Sn electrodes (Fig. 1). Interestingly, the Sn(100) electrode displayed a relatively small and sharp irreversible cathodic peak of -0.027 mA/cm^2 at 1.45 V during the first sweep, whereas Sn(001) showed a huge cathodic current maximum of -1.4 mA/cm^2 at 0.85V. The significant differences observed in reactivity toward electrolyte implied different reaction paths and product compositions or distributions as a function of Sn surface structure.

The corresponding *in situ* ellipsometry results suggested that a protective and stable SEI developed on the Sn(100) while the decomposition products formed on Sn(001) mostly dissolved away.

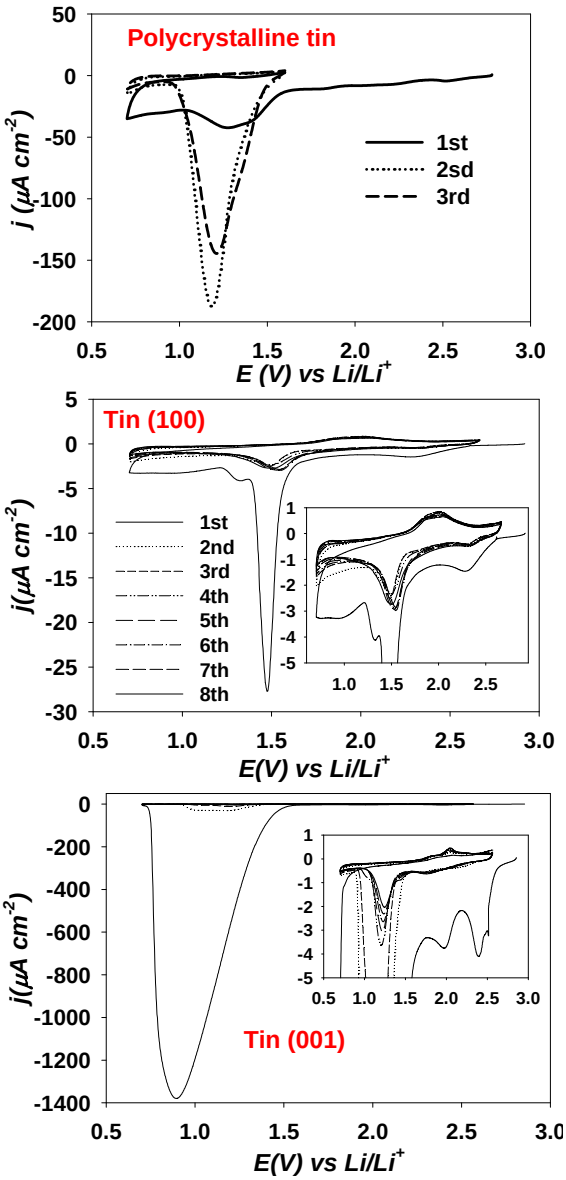


Figure 1. Cyclic voltammograms of polycrystalline and single crystal (100) and (001) tin electrodes in 1 mol L^{-1} $LiPF_6$ EC: DEC (1:2, w:w): 1mVs^{-1}

Decomposition products of high molecular weight (diethyl-2,5-dioxahexane dicarboxylate type) were identified in high concentrations in the electrolyte after prolonged galvanostatic polarization of polycrystalline Sn at 1.3 V. Such compounds, usually occurring after thermal degradation of the electrolyte, could have been produced *via* an electrochemical-chemical reaction scheme, as previously proposed for Li-ion carbonaceous anode materials. Preliminary experiments carried out in electrolytes of different compositions tended to indicate that both DEC and PF_6^- are possible precursors of the cathodic irreversible processes observed on the Sn electrode. These results suggest that both electrolyte composition and electrode surface structure must be optimized in unison to achieve long-term interfacial stability for intermetallic anodes. This report confirms the completion of milestone (b).

TASK 5.2 - PI, INSTITUTION: Xiao-Qing Yang, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: Low voltage, high stability: Gr/1 M $LiPF_6$+EC:DEC (1:2)/$LiFePO_4$
High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIER: PHEV: energy density, cycle life; HEV: power density, abuse tolerance.

OBJECTIVES: The primary objective is to determine the contributions of electrode material changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density Li batteries with better safety characteristics and longer life. The second objective is to design, synthesize, and characterize new electrolytes for PHEV oriented high-energy-density Li/air batteries. Special attention will be given to the new non-aqueous electrolytes with the capability to dissolve Li_2O and Li_2O_2 oxides for Li/air batteries. Testing facilities for high energy Li/air cells and the testing cells using these new, non-aqueous electrolytes, as well as gas diffusion electrodes for Li/air cell will be constructed and investigated at UMASS Boston.

GENERAL APPROACH: Our approach is to use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft XAS will be used to distinguish the structural differences between surface and bulk of electrodes. Time-resolved, X-ray diffraction (TRXRD) will be used to understand the reactions that occur in charged cathodes at elevated temperatures. *In situ* XRD with PSD detector will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at various C rates. These approaches developed at BNL will be available to other BATT members through extended collaboration. For the task of high-energy, lithium-air cells, our approach is to combine the two strengths at BNL, the organic synthesis and *in situ* characterization with the expertise of air-metal batteries at UMASS Boston to reach the proposed objectives.

STATUS OCT. 1, 2009: We have completed the studies on the structural characteristics in one type of the $LiFe_{1-x}M_xPO_4$ (M=Mn, Co, and Ni) phosphate cathode materials using various synchrotron X-ray techniques. The study of this material, $LiFe_{0.25}Mn_{0.25}Co_{0.25}Ni_{0.25}PO_4$ has been completed using *in situ* XRD and XAS spectroscopies.

EXPECTED STATUS SEP. 30, 2010: We will continue our studies on the structural characteristics of different types of $LiFe_{1-x}M_xPO_4$ (M=Mn, Co, and Ni) phosphate cathode materials using various synchrotron X-ray techniques. We expect to complete the structural study on the $LiFe_{1-x}Mn_xPO_4$ using *in situ* XRD and XAS spectroscopies. We will start our Li/air battery studies in non-aqueous electrolytes with gas diffusion electrodes made of carbon materials with various morphologies.

RELEVANT USABC GOALS: 15 year life, <20% capacity fade.

MILESTONES:
(a) Complete XAS studies of $LiFe_{1-x}Mn_xPO_4$ (x=0 to 1) cathode materials during electrochemical cycling. (Apr. 10) **Complete**
(b) Complete the preliminary studies of carbon structure effects on the electrocatalysis performance of air cathode in Li/air cells. (Apr. 10) **Complete**
(c) Complete *in situ* x-ray diffraction studies of $LiFe_{1-x}Mn_xPO_4$ (x=0 to 1) cathode materials during electrochemical cycling. (Sep. 10) **Complete**
(d) Complete the design and construction of Li/air testing cell. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

In situ structural studies of carbon-coated, mesoporous, $LiFe_{1-x}Mn_xPO_4$ ($0.0 \leq x \leq 1.0$) cathode materials were carried out using synchrotron based X-ray techniques (*e.g.*, XRD and XAS). This led to better understanding of the phase-transition mechanism during Li extraction/insertion, which in turn, provided useful information about how to achieve high performance and cyclability. All of the milestones proposed in the FY 2010 AOP were completed in quarter 4.

In the 4th quarter of FY 2010, *in situ* XRD studies on a series of nano-porous olivine $LiFe_{1-x}Mn_xPO_4$ ($0.0 \leq x \leq 1.0$) cathode materials were completed in collaboration with Prof. Li at the Institute of Physics, Chinese Academy of Sciences. The results of the studies showed that the structure changed from the lithiated phase of $LiFe_{1-x}Mn_xPO_4$ (original phase O-P) to the intermediate phase (I-P) first, and then to the fully delithiated phase of $Fe_{1-x}Mn_xPO_4$ (final phase, F-P). However, the phase transitions from O-P to I-P and from I-P to F-P did not start at the beginning of the voltage plateaus, as expected for the equilibrium situation, but near the end of the plateaus, where the voltage was rising rapidly. As shown in Fig. 1, for the *in situ* XRD patterns of the $LiFe_{0.6}Mn_{0.4}PO_4$ sample collected during the first charge at a C/12 rate, the I-P was observed at the end of the first plateau and the F-P was observed at the end of the second plateau. For the XRD patterns shown in Fig. 2, for the $LiFe_{0.8}Mn_{0.2}PO_4$ sample collected during the first charge at C/12, the formation of I-P and F-P moved to later stages of the charging curve as compared with those in Fig. 1 and were synchronized with the sharp increase of voltage at the end of the corresponding voltage plateaus. These interesting phenomena will be studied further in 2011.

In collaboration with Prof. Qu and his team at the University of Massachusetts (UMASS) at Boston, the milestone for the Li/air battery proposed for the 4th quarter of FY 2010 was completed. The Li/air cells were designed and constructed. Using these cells, the effects of surface modifications targeted to prevent passivation of the carbon surface as a result of the deposition of Li_2O and Li_2O_2 were studied. A manuscript based on these studies was submitted to the scientific journal "Carbon".

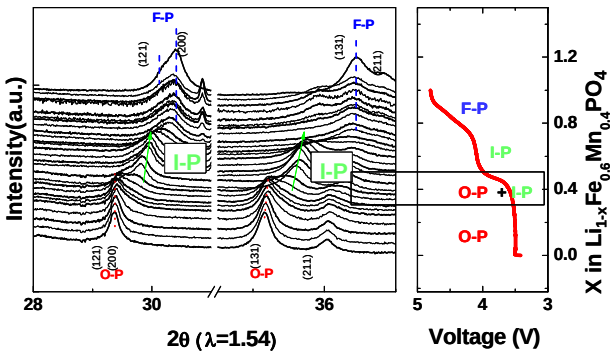


Figure 1. Charge-discharge curves (right panel) and *in situ* XRD patterns (left panel) of $LiFe_{0.6}Mn_{0.4}PO_4$ during first charge.

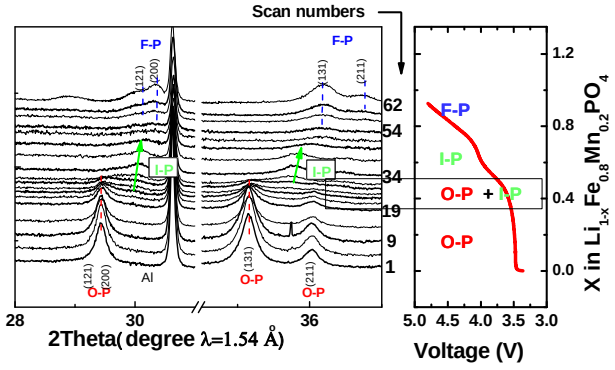


Figure 2. Charge-discharge curves (right panel) and *in situ* XRD patterns (left panel) of $LiFe_{0.8}Mn_{0.2}PO_4$ during first charge.

TASK 5.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, Stony Brook University

TASK TITLE - PROJECT: Diagnostics - First Principles Calculations and NMR Spectroscopy of Electrode Materials

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
High voltage, high power: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiMn_2O_4$
Low voltage, high stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Low, rate capabilities; high cost; poor stability; low energy-density

OBJECTIVES: Determine the effect of structure on stability and rate capability of cathodes and anodes. Explore relationship between electrochemistry and particle size and shape. Develop new, stable, cathode materials with high energy-density.

GENERAL APPROACH: Use solid state NMR and diffraction/TEM to characterize local and long-range structure as a function of particle size, sample preparation method, state of charge and number of charge cycles (cathodes). Use electrochemistry to correlate particle size with rate performance. Continue to develop the use of *in situ NMR* methods to identify structural changes and reactivity in oxides and intermetallics. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure and particle size on cell voltages and rate capability. Use high-throughput computing to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT 1. 2009: *In situ* NMR and XRD experiments will be ongoing. Diffusion calculation methodology established. High-throughput search enabled.

EXPECTED STATUS SEP. 30, 2010: Silicon structural studies will be complete. Olivine phase transformation kinetics study will be complete.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:
(a) Obtain size effect on Li mobility in olivines. (Mar. 10) **Complete**
(b) Initiate Li mobility calculations in other materials such as graphite and spinel. (Mar. 10) **Complete**
(c) Identify potential new electrode materials for synthesis experiments. (Mar. 10) **Delayed, due Mar. 11**
(d) Complete Si PDF data. Initiate *in situ* NMR studies of multicomponent electrodes (Mar. 10) **Complete**
(e) Identify pathways for charge/discharge reactions in olivines and materials with first order transitions. (Sep. 10) **Delayed, due Mar. 11**
(f) Perform relevant experiments to test proposed mechanisms for doped phosphates. (Sep. 10) **Delayed, due Mar. 11**
(g) Identify potential new electrode materials for synthesis experiments. (Sep. 10) **Complete**
(h) Complete analysis of Si nanoparticles. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Structural Model for the Lithiation of Silicon. Lithium-ion batteries (LIBs) containing Si negative electrodes have been the subject of much recent investigation because of the extremely large gravimetric and volumetric capacities of Si. Recent work saw the completion of our *ex situ* ^{7}Li NMR studies and pair distribution function (PDF) analysis of X-ray data to investigate the changes in short range order that occur during the initial discharge (lithiation) and charge (delithiation) of Si. In particular, some of the local structures that are responsible for the distinct electrochemical signatures that are seen in the electrochemical profiles were identified. Lithiation of crystalline Si, on the 1st discharge, starts and progresses with bond breakage of the Si matrix to form both lithiated, isolated Si anions and lithiated Si clusters surrounded by Li^{+} ions. Once all of the bulk crystalline Si is consumed and total amorphization is achieved, the remaining Si clusters are broken to form predominantly fully-lithiated, isolated Si environments. Key to this mechanism is (i) the difficulty associated with Si-Si bond rupture, in that it is kinetically more favorable to lithiate Si clusters and form isolated Si ions, or form smaller clusters, than to break up the Si framework. (ii) Since a distribution of different Si clusters and anions are formed, the expected (more thermodynamically stable) crystalline phase based on the Li:Si ratio of the amorphous component, does not readily nucleate, since this would involve Si-Si bond breakage and rearrangement of the clusters. Only when essentially all of the Si clusters are broken up below 50 mV is it possible to nucleate a crystalline phase comprising isolated Si ions. The mechanism for delithiation to form the fully-delithiated phase progresses from a small number of nuclei, which are either formed on delithiation or which may still be present in the fully-discharged (lithiated) phase. These nuclei grow directly to form the amorphous (delithiated) Si phase without (significant) formation of any intermediate structures or compositions with multiple small clusters. The amorphous Si phase formed on the top of charge contains Si tetrahedra, but no or little order beyond the Si 2nd coordination shell (Fig. 1). The amorphous Si matrix is much more open, so that the *whole* matrix can now be partially lithiated at the end of the higher voltage process (*i.e.*, with a much lower overpotential than required to break the original crystalline framework), with only partially breaking down the Si network. The lower electrochemical process is associated with a breakage of the remaining smaller lithiated Si clusters, and it again ends with recrystallization of the fully-lithiated phase. If a partially-delithiated phase, and one that still contains Si clusters, is delithiated, these clusters appear to serve as nucleation sites, allowing the system to retrace a similar electrochemical pathway to that seen on discharge (lithiation). In contrast, if lithiation proceeds to form $Li_{15}Si_5$, *i.e.*, the phase with isolated anions, there are few Si nucleation sites, and delithiation proceeds *via* the growth of only a few Si clusters to form larger Si domains and eventually the amorphous Si phase. The results confirm that it is important to control the potential windows over which the material is cycled to optimize both the numbers and type of clusters that are formed and that this may affect the reversibility and rate performance of this system.

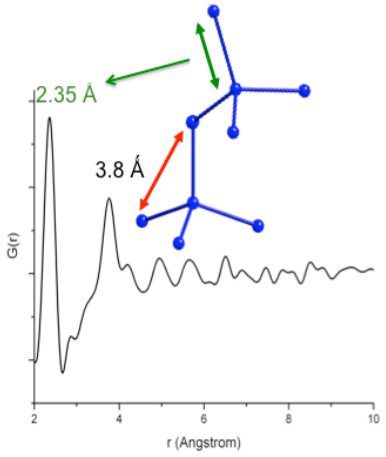


Figure 1. The pair distribution function (PDF) (G(r) of silicon following 1 cycle, obtain from diffraction data. The 1st two dominant correspond to directly bound Si and Si within a tetrahedral.

Novel Materials: Our computational search for novel cathode materials has resulted in several new potential cathode materials. Two of these are currently under extensive development and testing.

Task 5.4 - PI, INSTITUTION: Yang Shao-Horn, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Diagnostics - Studies and Design of Chemically and Structurally Stable Surfaces and Structures of Lithium Storage Materials

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIER: High cost, poor cycle and calendar life and abuse tolerance of Li-ion batteries

OBJECTIVES: To develop high-energy and long-cycle-life cathodes.

GENERAL APPROACH: The surface chemistry, microstructure of oxide-electrolyte interface with and without surface modification, and oxide crystal structure will be examined by scanning TEM, synchrotron XRD and XAS, and XPS. These surface and structural features and their changes during electrochemical measurements would provide insights into the nature of interfacial stability between oxide and electrolyte and developing strategies in the design of stable interfaces for high-energy and long-cycle-life cathodes.

STATUS OCT. 1, 2009: Changes in the surface chemistry of quenched and annealed $LiNi_{0.5}Mn_{0.5}O_2$ electrodes upon cycling to high voltages have been identified and compared with those of $AlPO_4$-coated $LiCoO_2$. Application of fundamental insights to design of new and stable surfaces for high-energy cathodes will be ongoing.

STATUS SEP. 30, 2010: The surface chemistry comparison of pristine and cycled $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCoO_2$ as a function of depth from surface using angle-resolved XPS will be complete, from which a working hypothesis on surface species stabilizing the cathode surface will be proposed. Preliminary experiments to test the working hypothesis by modifying the surfaces of high-energy cathodes to enhance cycle life will be complete.

RELEVANT USABC GOALS: High Energy/Power Ratio Battery, energy density (>100 Wh/kg, power density (>400 W/kg), 15-year calendar life and cycle life (5,000 cycles).

MILESTONES:
(a) Develop and demonstrate angle resolved X-ray photoelectron spectroscopy (ARXPS) to study the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCoO_2$ as a function of depth from surface. (Mar. 10) **Complete**
(b) Apply fundamental understanding of the relationship between the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCoO_2$ and cycle characteristics to design and develop stable surfaces of cycled high-energy cathodes including $LiNi_xMn_xCo_{1-2x}O_2$. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Angle-resolved XPS (ARXPS) was used to investigate the surface chemistry of LNMO composite cathodes after 20 cycles at C/5 between 2.0 and 4.6 V with a 4h hold at the top of charge. The cells consisted of Li counter electrodes and $LiPF_6$ in EC:DEC. The LNMO was prepared by quenching from 1000°C followed by annealing in air at 700°C for 12 h. The electrodes were transferred from an Ar-filled glovebox to the test chamber of the XPS spectrometer without exposure to ambient conditions. They were characterized as-is and after washing with the solvent of the electrolyte to remove excess electrolyte and other species loosely affixed to the surface. The ARXPS spectra were collected for the Li 1s, C 1s, O1s, F1s, P2p, Ni 2p and 3p, and Mn 2p and 3p regions but only those of Ni 2p and Mn 2p regions are provided in Fig. 1. The Ni and Mn $2p_{3/2}$ binding energies for the unwashed electrodes of 857 to 858 eV and 644 eV, respectively, were significantly higher than those reported for the powder material, indicating that surface Ni and Mn were present in highly-oxidized states after cycling in $LiPF_6$. Such high binding energy for Ni is close to that reported for $NiF_2{\cdot}4H_2O$ (857.3 eV), indicating the possible formation of Ni fluorides. This assignment can be supported by the Ni shake-up structure, the lack of lattice oxygen in the O 1s spectrum, and the presence of a fluorine component that corresponded to the formation of metal fluorides. The binding energy for Mn of *ca*. 644 eV was significantly higher than those reported for simple Mn oxides as well as fluorides (642.4 eV for both MnF_2 and MnF_3). Higher binding energies relative to those of simple oxides and fluorides have been reported for $MnSO_4$ (644.7 eV) and $KMnO_4$ (646.8 eV). Clearly, the chemistry of surface Mn is complex and requires further examination. On the other hand, the Ni and Mn $2p_{3/2}$ binding energies for the washed electrodes were significantly shifted lower relative to those for the unwashed electrodes. The Ni $2p_{3/2}$ binding energy of *ca*. 855 eV was consistent with those observed for Ni^{2+} in active material or NiO. The Mn $2p_{3/2}$ binding energy of *ca*. 642 eV was close to that of Mn^{4+} in active material but the presence of other forms of manganese oxides could not be ruled out. Thus, it was concluded that the surfaces of unwashed electrodes contained surface Ni and Mn in highly-oxidized forms that were loosely attached to the surface and easily removed by rinsing the electrodes with the solvent.

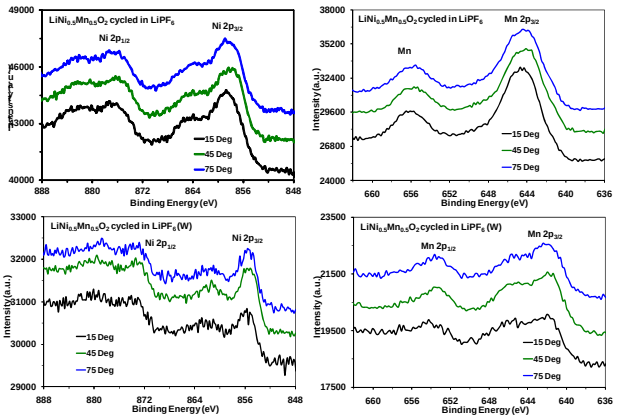


Figure 1. ARXPS of Ni and Mn 2p spectra for $LiNi_{0.5}Mn_{0.5}O_2$ electrodes cycled in $LiPF_6$ electrolyte before and after washing by the solvent.

In addition to the investigation of Ni- and Mn-based transition metal oxide cathodes, efforts were started toward developing a high-energy-density Li/Li_2O_x (x = 1, 2) rechargeable battery. Recent work (*Shao-Horn et al., ESSL, 2010*) demonstrated the ability of certain catalysts to oxidize Li_2O_2 into oxygen and Li ions. The utilization of Pt nanoparticles on a carbon support substantially decreased the overpotentials needed for charging the Li/Li_2O_2 cell. Further investigations of the catalytic activity of various metal and metal oxide materials toward the decomposition of Li_2O_x will be pursued in 2011.

Collaborations: Collaborations continue with M.M. Thackeray in using TEM to study the atomic structure of composite cathode materials.

BATT TASK 6
MODELING

TASK STATUS REPORT

TASK 6.1 - PI, INSTITUTION: John Newman, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Low voltage, high stability: Gr/1 M $LiPF_6$+EC:DEC (1:2)/$LiFePO_4$
High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Poor transport properties, capacity, and power fade

OBJECTIVES: Develop experimental methods for measuring transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

GENERAL APPROACH: Use simulations to improve understanding of limitations in cell performance. Develop improved experimental methods for measuring transport and kinetic properties.

STATUS OCT 1, 2009: Characterization of the $Li_xTi_5O_{12}$ interface will be complete. Comparisons between redox shuttle behavior against $Li_xTi_5O_{12}$ and graphite electrodes will be ongoing. Rotating disk experiments will be ongoing.

EXPECTED STATUS SEP. 30, 2010: Experiments comparing the kinetics of different redox shuttles through passivating films on inert surfaces will be ongoing. Modeling the effects of impurities in lithium-ion batteries will be ongoing. Another new project studying anion alternatives to PF_6^- will begin.

RELEVANT USABC GOALS: 5000 deep discharge cycles; 15 year calendar life

MILESTONES:
(a) Measure kinetics of ferrocenium reduction through passivating films on an inert electrode surface. (Dec. 09) **Complete**
(b) Identify key components and reactions to model. (Feb. 10) **Cancelled due to change in direction to concentrate on modeling shape changes in lithium electrodes.**
(c) Compare reduction kinetics of different redox shuttles on inert surfaces. (Apr. 10) **Delayed until August 2011 due to experimental difficulties and new results.**
(d) Initiate kinetic studies using either highly-ordered-pyrolytic-graphite or composite graphite electrodes to approximate more closely conditions in a real cell. (Jul. 10) **Initiated on time. Because no useful results were obtained, this milestone was canceled and emphasis placed on (a) and (f)**
(e) Determine effects of added impurities to Gr/$LiFePO_4$ system. (Sep. 10)- **Cancelled due to change in direction to concentrate on modeling shape changes in Li electrodes**.
(f) Construct 2-D model of Li-metal redistribution. (Aug. 10) **Complete**

PROGRESS TOWARD MILESTONES

Expected status Sep 30, 2010

Several of the milestones set at the beginning of FY10 underestimated the difficulties associated with experimental nonaqueous electrochemistry. Because reproducible data for the through-film reduction of ferrocene was not obtained until the Summer of 2010, milestones (a) and (c) were delayed, while (d) was canceled due to the importance of focusing on inert systems. Additionally, a planned project on modeling the effect of battery impurities (milestones (b) and (e)) was replaced with a project modeling shape changes in Li electrodes (milestone (f)).

Modeling Shape Changes in Lithium Electrodes:

Previous work developed a model of the two-dimensional shape change of a Li negative electrode along its length incorporating both kinetic and transport limitations (please refer to the Q3 FY 2010 BATT report for more information). Further work will be done to increase the number of cycles for which the simulation is run, to increase the depth of discharge of a cycle, and to include pressure and temperature effects.

Interaction of Redox Shuttles and the SEI

After much work, the reduction current of ferrocene through a passivating film was measured and a model developed to fit the data. Both measurements and model fits are shown in Fig. 1. The markers show the kinetic current intercept of a Koutecký-Levich plot after films were formed on the electrode for 10, 30, and 60 minute holds at 0.6 V. As the lines show, the current decreased with passivation time because the electrode had more time to grow a "thicker" film. The model includes only three adjustable parameters: a transfer coefficient α, an exchange current density i_0, and a through-film ferrocene limiting current i_{lim}, given below.

$$i_0 = k\varepsilon^2 (C_O^{bulk})^{\alpha_c} (C_R^{bulk})^{\alpha_a} \qquad i_{\lim} = \frac{-FD_{O,f}\varepsilon C_O^{bulk}}{L}$$

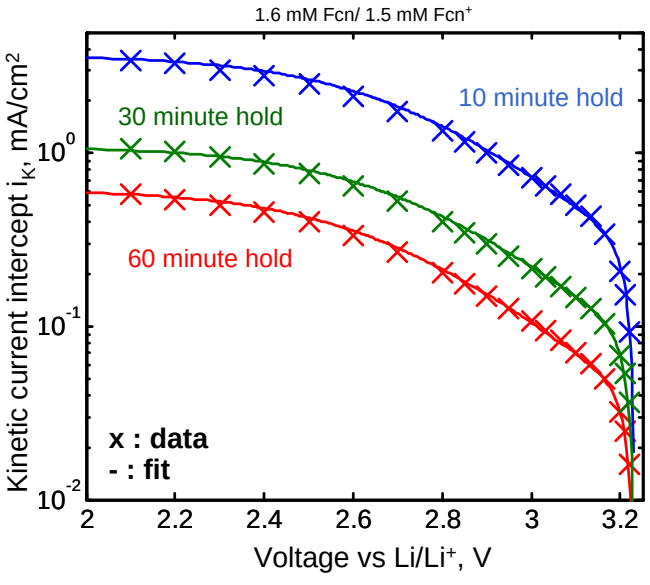


Figure 1. Kinetic current (from Koutecký-Levich plots) *vs.* voltage after different lengths of passivation holds. Both i_0 and i_{lim} decrease.

The slope of the linear region between 3.15 and 2.8 V is given by α, while the intercept of that line with 3.22 V (open circuit) is i_0. i_0 was not expected to depend on film thickness. i_{lim} is the limit as the curve approaches very low voltages and should decrease with film thickness. However, because both expressions contain the porosity, ε, an alternative possibility may be that longer formation times cause thicker but also less porous films. More work is required to verify this explanation, and nonelectrochemical characterization is currently being considered. An abstract on this subject was presented at the annual ECS meeting, Las Vegas, October 2010.

TASK 6.2 - PI, INSTITUTION: Venkat Srinivasan**,** Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling - Mathematical Modeling of Next-generation Li-ion Chemistries

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/1 M $LiPF_6$+EC:DEC (1:2)/$LiFePO_4$

BARRIERS: High cost (or low energy)

OBJECTIVES:
1. Quantify the usefulness of alloy anodes for use in PHEVs.
2. Understand behavior and suggest means to enhance performance of high-energy phosphates (*e.g.,* $LiMnPO_4$).

GENERAL APPROACH: Develop mathematical models for candidate Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to connect fundamental material properties to performance and provide guidance to material-synthesis and cell-development PIs. Use models to quantify the ability of the candidate chemistry to meet DOE performance goals.

STATUS OCT 1. 2009: The model that describes the kinetic behavior of Si anodes will be compared to data from nanopowder laminates. The kinetic parameters extracted from laminates will be compared to the parameters extracted from the thin-film experiments.

EXPECTED STATUS SEP. 30, 2010: The model for Si anodes that describes thermodynamic, kinetic, and mass transfer effects will be complete. However, the model will not include stress effects and the associated cracking of the particles. The model will be used to guide the experimental work on the use of Si nanopowder as electrodes. The impact of coating the surface of the Si with Cu will be studied to understand if this provides a path to increase the cycle life of alloys.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10-s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile).

MILESTONES:
(a) Quantify the improvement in cycle life, if any, of silicon thin-film with and without a layer of copper and find the optimum copper thickness to enhance life without scarifying power. (Jan. 10) **Complete**
(b) Coat copper on nanopowders of silicon and test laminates and quantify performance improvements, if any. (Mar. 10) **Complete**
(c) Identify conditions (*i.e.,* current, particle size etc.) under which $Li_{15}Si_4$ forms during charging of silicon anodes and compare to the PHEV goals to access effect of PHEV cycling on performance. (Jul. 10) **Complete**
(d) Develop model for the Si/NCM system to compare to the baseline. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

Modeling silicon anodes: Over the last fiscal year we have developed a model for a Si anode. The model takes into consideration the various complications that exist in this system including the two-phase region, the significant volume change on cycling, in addition to thermodynamic, transport, and kinetic effects. Also taken into consideration are the porous nature of the electrodes, the decrease in pore volume as the particles expand, and the concomitant electrolyte displacement. Over the last quarter we started simulations on this system by designing electrodes to match it to a NCA cathode of 80 µm thickness and 35% porosity. The NCA cathode (capacity: 180 mAh/g) is chosen instead of the NCM cathode (160 mAh/g) material because of the higher system energy.

The matching of the anode to cathode was performed for various cycling capacities for the Si (1000, 2000, and 3000 mAh/g) and simulations were conducted to understand the effect of rate on the charging of the anode and the associated concentration effects. The effect of the various losses in the battery is captured in Fig. 1. which shows a Peukert plot for the anode operating under different capacities. In each case the initial anode porosity is chosen so that the porosity in the fully charged state is 25% and the thickness of the anode is calculated by matching it to the cathode capacity. Therefore, the anode thickness is higher for 1000 mAh/g cycling compared to 3000 mAh/g cycling.

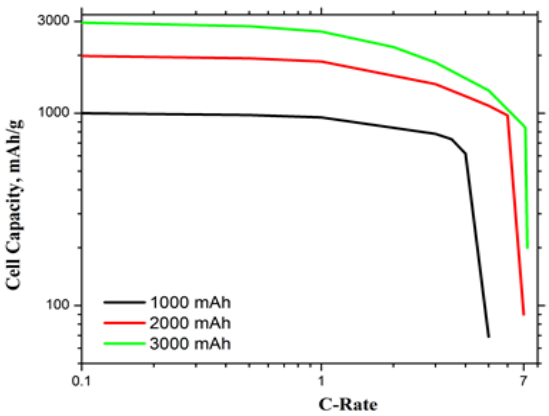


Figure 1. Rate capability of cells charged to 1000, 2000, and 3000 mAh/g with the capacity matched to a NCA cathode of 180 mAh/g capacity, 80 µm thick, 35% porosity loading.

Figure 1 shows three distinct regions (i) at low rates where no loss in utilization occurs, (ii) at intermediate rates where the anode is limited by solid-state mass transfer in the Si particles and (iii) at high rates where the electrode is limited by liquid phase transport. As the charging current is increased, the reaction distribution moves to the separator/electrode interface thereby leading to a larger volume change in this region, resulting in clogging of the pores. This effect becomes more pronounced at lower capacities of cycling the Si due to the larger thickness of the anode. The milestone is therefore complete.

This model will be extended to calculate the volumetric energy density and the impact of the electrolyte volume effects.

Mechanical degradation in Li-ion battery electrodes: This fiscal year, a mathematical model to understand the mechanical degradation in electrodes was developed. While literature studies of mechanical degradation have considered only the active material, we include the interaction of binder and active material. The model has been used to understand cycling conditions under which cracking of the particles and the binder can occur. Our results indicate that incorporation of binder interaction is important in failure analysis.

We have also looked at the effect of stress during varying cycling protocols. One such cycling condition, in which the electrode is subjected to an open-circuit relaxation during a constant current discharge, clearly shows the importance of incorporating the binder interaction in correctly simulating stress effects in Li-ion batteries.

The model is presently being expanded to describe both cathode and anode materials and to provide guidance on design on batteries to minimize mechanical degradation.

TASK 6.3 - PI, INSTITUTION: Ann Marie Sastry, University of Michigan, Ann Arbor

TASK TITLE - PROJECT: Modeling - Thermo-electrochemistry, Capacity Degradation, and Mechanics with SEI Layer

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIER: Prediction of capacity degradation, and excessive conductive mass which penalizes energy and power density and increases cost.

OBJECTIVES: (i) multiphysics FE modeling considering thermal effects, (ii) modeling of SEI layer formation, (iii) measurements of SEI layer properties

GENERAL APPROACH: Multiphysics finite element models of cells will be extended in order to evaluate stress distribution and the heat generation, toward prediction of lifetime. The formation and morphology changes in SEI films during the first electrochemical intercalation of Li ion into electrode will be modeled as a precipitation process including a nucleation phase and phase growth involving the precipitation of new phases. Also, we will utilize experimental techniques such as XPS, Raman, TEM, and AFM to measure the properties of SEI layer depending on cycling, charge/discharge rate, and temperature.

STATUS OCT. 1, 2009: Integration of thermal and kinetic effects has allowed extension to many particle geometries and consideration of many types of packing architectures. Completion of the integration of mechanics analysis has allowed consideration of mechanical loads in the context of realistic failure loads in binders and ceramic particles. SEI consideration is well underway, and the initial simulations of effect of layering will be complete.

EXPECTED STATUS SEP. 30, 2010: We expect to extend and/or establish (1) multiscale FE model considering thermal effects, (2) SEI layer formation model, and (3) characterization methodologies to study the SEI layer validating models under development. Capacity degradation of Li ion battery on graphitic materials (mainly used as anode for commercial Li-ion battery) can be correlated to the variation of SEI layer including composition, internal structure, and mechanical strength.

RELEVANT USABC GOALS: *Available energy for CD mode*: 3.4 kWh (10 miles) and 11.6 kWh (40 miles); *Cycle life*: 5000 cycles (10 miles) and 300,000 cycles (40 miles); *10- s discharge power*: 45 kW (10 miles) and 38 kW (40 miles); *Calendar life*: 15 years (40°C).

MILESTONES

(a) Implement multiphysics FE model for thermo-electrochemistry. (Mar. 10) **Complete**
(b) Implement SEI formation modeling. (May 10) **Complete**
(c) Measure SEI properties to inform these models (Aug. 10) **Delayed, due Jun. 11**

PROGRESS TOWARD MILESTONES

This project consists of three separate, but synergistic, research topics focused on better understanding of the SEI layer: two topics take a computational approach and the third focuses on experimental work to characterize the SEI layer. The following is a summary of research activities on each topic during the fourth quarter (July 1 to September 30, 2010):

1) **Multiphysics FE model for thermo-electrochemistry** (implemented)
Surrogate models of closure terms (*i.e.*, reaction current density and heat generation) were constructed for the 3D-microscopic model shown in Fig. 1. Face-centered composite design (FCCD) and Latin hypercube sampling (LHS) were used to generate a set of simulation points as design of experiments (DOE). Surrogate models were generated *via* the kriging method. Prediction error sum of squares (PRESS) of constructed surrogate models for reaction current density and heat generation were 0.038 and 0.023. Figures 2 and 3 show the global sensitivity analysis results of reaction current density and heat generation with respect to Li-ion concentrations, electric potentials, and temperature.

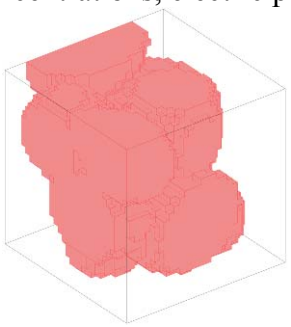


Figure 1

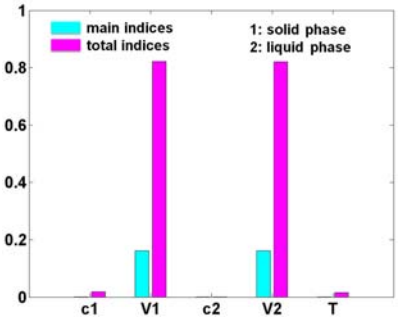


Figure 2

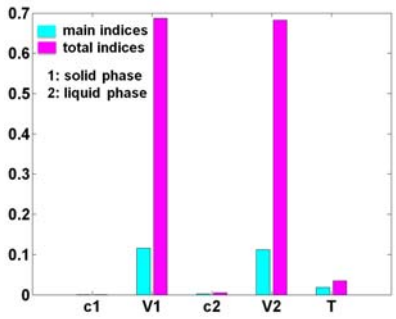


Figure 3

2) **SEI formation modeling** (implemented)
A phase field model integrating the chemical energy and interfacial energy was developed to account for the SEI layer growth process. Figure 4 shows the schematic representation of SEI layer formation. Figure 5 shows the results of the phase field model. In step 1, depending on the surface energies between each species, the final equilibrium angle varied. In step 2, the layer could grow further when more organic compounds deposited on the developed layer.

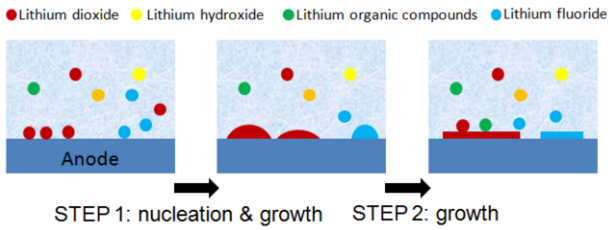


Figure 4

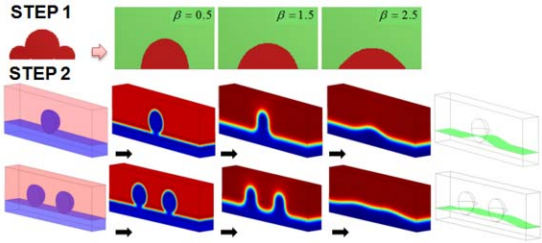


Figure 5

3) **Measurement of SEI properties** (current status)
(i) Mechanical properties: iCon AFM with PeakForce QNM developed by Veeco can provide high-resolution modulus mapping as well as deformation and adhesion: installation of this instrument was recently completed and it is now ready to be used for this research in EMAL at UM. Training of personnel is scheduled and modulus mapping of the SEI layer is set to begin.
(ii) Microstructure and chemical elements: Samples for IR and TEM analysis have been produced using a Swagelok cell using LMO composite electrodes. The theory and experimental plan were jointly discussed by the UM and ORNL teams. Planning is underway for the UM team to visit ORNL in order to carry out IR and TEM experiments and for further discussion of IR techniques.

BATT TASK 7

Research Investigators at Berkeley Lab

TASK 7.1 - INVESTIGATOR, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Advanced Binder for Electrode Materials

SYSTEMS: High-voltage, high-energy: Gr./1M $LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: High energy system: poor cycle life, high first cycle irreversible capacity, low coulomb efficiency.

OBJECTIVES: Develop new conductive polymer binder materials to enable large volume change silicon-alloy material to be used in lithium-ion negative electrode.

GENERAL APPROACH: Use functional polymer design and synthesis to develop new conductive polymers with proper electronic properties, strong adhesion and improved flexibility to provide electric pathways in the electrode, and to accommodate large volume change of the Si alloy active material during lithium insertion and removal.

STATUS OCT. 1, 2009: Developed one type of conductive polymer binder materials. Fabricated Si/conductive binder electrode, and tested this electrode against Li-metal counter electrode in a coin cell configuration. The electrode gives over 2000 mAh/g reversible capacity between 0.01 and 1V voltage range for 150 cycles at 99% Coulomb efficiency.

EXPECTED STATUS SEP. 30, 2010: Gain fundamental understanding of the functions of the conductive polymer in the Si electrodes; assess the pros and cons of the different methods to compensate for first-cycle loss of the Si/conductive polymer electrodes; and demonstrate full-cell cycling capability of the Si/conductive polymer negative electrode.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:
(a) Map out the doping process for the Si/conductive polymer in the composite electrode. (Apr. 10). **Complete**
(b) Characterize the conductivity of the conductive polymer binders. (Apr. 10). **Complete**
(c) Compensate for the first-cycle irreversible-capacity-loss of the Si electrode. (Sep. 10). **Complete**
(d) Fabricate and test lithium-ion cells based on the Si electrode. (Sep. 10). **Complete**

PROGRESS TOWARD MILESTONES

Milestone (a, b). Map out the doping process for the Si/conductive-polymer electrode. (Apr. 10, accomplished)

Milestone (c). Compensate for the first-cycle irreversible-capacity-loss of the Si electrode. (Sep. 10, accomplished)

Silicon-based electrodes tend to have high first-cycle irreversible-capacity-loss. The Si/conductive polymer electrode affords even higher irreversible capacity, due to the irreversible Li^+ doping of the conductive binder during the first lithiation. Stabilized Lithium Metal Powder (SLMP) from FMC was used as an anode additive to improve the first-cycle efficiency of the Si/conductive-polymer electrode. An effective method involving the addition of SLMP during the anode slurry fabrication process was developed. This approach allowed convenient introduction of Li into the negative electrode. The first-cycle efficiency could be systematically adjusted from 60 to 100%, as shown in Fig. 1, without compromising cycling ability.

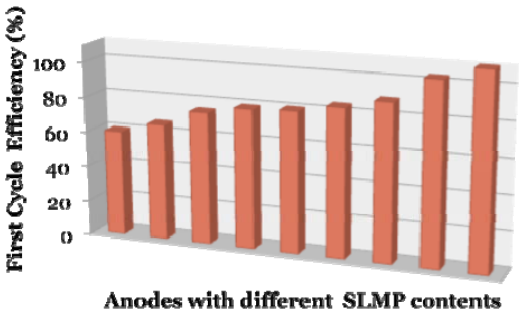


Figure 1: Improve 1st cycle coulombic efficiency by SLMP doping of the Si/conductive polymer anodes.

A patent disclosure was filed by the LBNL patent department. The Project Lead visited FMC in May to gain in-depth knowledge of the SLMP products.

Milestone (d). Fabricate and test Li-ion cells based on the Si electrode. (Sep. 10, accomplished)

Different types of Si electrodes developed in milestone (c) were used to fabricate Li-ion cells using a standard positive electrode of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (L333). Figure 2 shows the initial 25 cycles of a Si/L333 cell. The Si electrode was formed by first cycling it against a Li-metal counter electrode in a separate cell. The Si electrode was then coupled with a L333 positive electrode to form a full Li-ion cell. The significant capacity fade may be a result of the loss of cycleable Li from side reactions with the electrolyte on the Si surface. Such reactions are reflected in the coulombic efficiency, also plotted in Fig. 2.

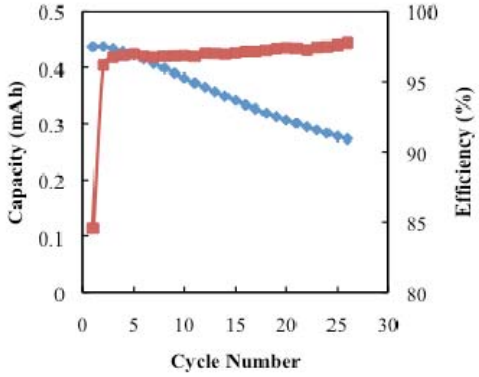


Figure 2: Cycling behavior of Si/L333 full cell.

Collaborations: Vince Battaglia, Venkat Srinivasan, Wanli Yang (ALS), Lin-wang Wang (MSD).

TASK 7.2 - INVESTIGATOR, INSTITUTION: Guoying Chen, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: High-Energy Cathodes - Improving Performance, Safety, and Cycle Life through Crystal Structure and Particle Morphology Design

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
Low-voltage, high-stability: Gr/1 M $LiPF_6$+EC:DEC (1:2)/$LiFePO_4$

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000 cycles/58 MWh).

OBJECTIVES: Explore phase transition mechanisms and kinetic barriers of high-energy cathode materials. Establish direct correlations between crystal structure, composition, morphology, performance, and stability. Provide guidelines to design and fabricate cathode materials with improved energy density, rate capability, and safety, especially with regard to thermal stability.

GENERAL APPROACH: Prepare well-formed crystals with various structure, composition, size, and morphology using soft chemistry synthesis routes, such as hydrothermal and solvothermal reactions. Characterize their physical properties and investigate their solid state chemistry using advanced spectroscopic, spectromicroscopic, scanning calorimetry, and electron microscopic techniques.

STATUS OCT. 1, 2009: Mg-substitution in $LiMnPO_4$ crystals was found to improve the delithiation kinetics. The effect of the substitution has been investigated, and the optimal Mg-substitution level was determined to be 20%. Chemical or electrochemical delithiation of $LiMnPO_4$ results in the formation of a solid solution phase, Li_yMnPO_4 ($y < 0.16$), whose lattice parameters depend upon the global extent of delithiation and on the crystalline domain size of the delithiated phase. The delithiated Li_yMnPO_4 was found to be thermally unstable. It decomposes to release O_2 and exhibits strong exotherms in the presence of a Li-ion electrolyte, comparable to the behavior of charged $LiCoO_2$ electrodes under similar conditions.

EXPECTED STATUS SEP. 30, 2010: New approaches to improve thermal stability and performance of $LiMnPO_4$ will have been explored. Synthesis routes to prepare discrete crystals of layered oxides containing Ni, Co, and Mn will have been investigated.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD)

MILESTONES:
(a) Report thermal stability and performance evaluation of the modified $LiMnPO_4$. (Mar. 10) **Complete**
(b) Report results on the synthesis of layered oxide crystals. (Aug. 10) **Complete**

PROGRESS TOWARD MILESTONES

Phosphates: It was previously demonstrated that Mg substitution of Mn improved the kinetics of $LiMnPO_4$ during chemical delithiation and relithiation, with the best performance achieved with 20% Mg substitution. To complete the study in this series, electrochemical performance of $LiMg_xMn_{1-x}PO_4$ (x=0, 0.1 and 0.2) composite electrodes was compared in this quarter. Potentiostatic intermittent titration tests (PITT) were used to charge and discharge the highly-resistive, large, phosphate crystals under near-equilibrium conditions. Figure 1 shows the obtained incremental capacity ($\Delta Q/\Delta V$) at a potential step of 10 mV. With increasing Mg content, the charging potential gradually shifted toward high voltage, while the discharge potential remained nearly constant. $LiMg_{0.2}Mn_{0.8}PO_4$ delivered the highest integrated charging capacity of 150 mAh/g, as compared to the 100 mAh/g acquired from the unsubstituted $LiMnPO_4$ material. This was consistent with results obtained for chemical delithiation. The columbic efficiency of all of the electrodes was low due to particle isolation as a result of not adding enough carbon coating on the crystals.

As part of the effort to improve the rate of $LiMnPO_4$, a thin surface layer of polytriphenylamine (PTPAn) was introduced by electropolymerization of 0.07 M triphenylamine in 1M $LiPF_6$ in 1:1:3 PC:EC:DEC electrolyte. PTPAn is an electroactive polymer that has been shown to have a reversible capacity of 110 mAh/g between 3 to 4.5 V and a high electronic conductivity of 0.1 S/cm upon oxidation to 4.0 V. The presence of an intimate conductive coating and the added capacity from the polymer may lead to improved performance of the $LiMnPO_4$-based electrodes. Unfortunately, PTPAn-treated hydrothermal $LiMnPO_4$ crystals delivered little reversible capacity, suggesting large resistance even in the presence of the conductive polymer. For the purpose of comparison, carbon-coated $LiMnPO_4$ from HPL was then used for the study. PTPAn was electrodeposited on these particles by cycling the cathode between 3 and 4.5 V 10 times in the solution containing the monomer precursor. This led to a coating layer equal to 10% of the total mass. The pristine and polymer-coated C-$LiMnPO_4$ powders were then assembled in "Swagelok" cells with Li as the anode and glass fiber as the separator, and were charged and discharged between 3 and 4.5V at constant current. The voltage profiles at various rates are compared in Fig. 2, with the capacity normalized to the total mass of the cathode powder. Improvements in reversible specific capacity and rate capability were achieved in the polymer-coated sample at low rates, with the discharge capacity increasing 30% at C/15 and 20% at C/8. The performance of the material, however, is still far from meeting the PHEV goals. This report completes the work toward milestone (a).

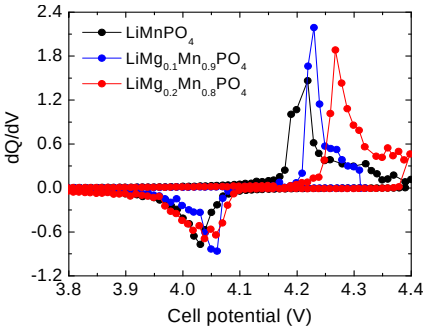


Figure 1. PITT data of $LiMg_xMn_{1-x}PO_4$ composite electrodes.

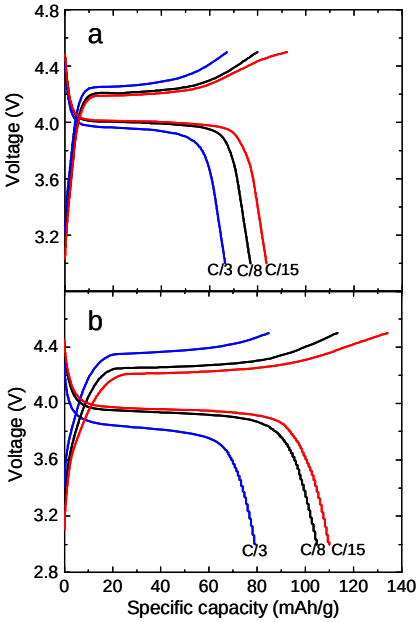


Figure 2. Charge and discharge profiles of the cells with a) HPL C-$LiMnPO_4$ and b) PTPAn-coated HPL C-$LiMnPO_4$ cathode.

Collaborations this quarter: Richardson, Kostecki, Doeff, and Cabana (LBNL); Nobumichi (ALS); NCEM; Grey (Stony Brook).

TASK 7.3 - INVESTIGATOR, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Positive and Negative Electrodes: Novel and Optimized Materials

SYSTEMS: Low-voltage, high-stability: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiFePO_4$
High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: Low-energy-density, poor cycle life, safety.

OBJECTIVES: Understand the relationship between particle size shape and electrode performance. Understand the chemical and physical phenomena behind the reactivity of negative electrode materials based on metal oxides. Design new materials that yield high capacities at high voltages. Develop new and engineered materials that can fulfill the energy/power density, cycle life, and safety requirements and goals of USABC.

GENERAL APPROACH: 1) Employ synthesis methods that lead to well controlled particle sizes and shapes to produce samples with different degrees of anisotropy. Evaluate their performance and correlate it with the microstructural features. 2) Use several characterization techniques (diffraction, spectroscopy, microscopy) to get a complete picture of the interactions that lead to reversibility, but poor cycle life in materials that electrochemically react with Li through conversion reactions. 3) Investigation of new phases that can react *via* a Cu extrusion mechanism while maintaining a stable framework that leads to enhanced cycle life. Evaluation of the effect of the framework on the voltage at which extrusion takes place.

STATUS OCT. 1, 2009: $LiNi_{1/2}Mn_{3/2}O_4$ has been prepared from hydroxide precursors and through a modified Pechini method, and the cycling performance at high rate has been evaluated. The first samples of $LiNi_{1/2}Mn_{3/2}O_4$ with different degrees of anisotropy have been prepared using solvothermal methods. Preliminary results of the electrochemical performance of $CuMoO_4$ and $CuAl_2O_4$ as electrode materials have been obtained. $CuMn_2O_4$ has been abandoned due to its poor reversibility.

EXPECTED STATUS SEP. 30, 2010: The performance of $LiNi_{1/2}Mn_{3/2}O_4$ made using solvothermal routes will have been evaluated. Nanometric Sn-based alloys with narrow particle sizes and shapes will have been prepared and tested. The chemical and physical phenomena, behind the good initial reversibility but poor extended cycle life of NiO, will have been studied by XAS, NMR and TEM. New promising Cu-M-O phases will be identified, synthesized, and tested.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles.

MILESTONES:
(a) Report the cycling performance of $LiNi_{1/2}Mn_{3/2}O_4$ made solvothermally. (Mar. 10) **Complete**
(b) Choose promising Cu-M-O (M=transition metal, Al, P, Si) phases and provide test results. (Jul. 10) **On going, due Sep. 11**
(c) Synthesize Sn-based nanoalloys with controlled microstructure and report their performance as electrodes. (Sep. 10) **Complete**
(d) Report the characterization of cycled NiO electrodes by NMR, XAS and TEM. (Sep. 10) **Complete, No-go decision**

PROGRESS TOWARD MILESTONES

Collaborations: Prof. Grey (SUNY Stony Brook), Drs. Persson, Battaglia, Milliron, Doeff, Richardson, Guo (LBNL), Dr. Casas-Cabanas (CRISMAT, France), Dr. Palacin (ICMAB, Spain).

Milestone A: This milestone was completed during the first quarter of the year, as scheduled.

Milestone C: Samples of Sn alloys with different particle sizes, ranging from hundreds to tens of nanometers were prepared. Due to delays with the setup of an electrochemistry laboratory, electrochemical testing has been suspended to FY 2011.

Milestone D: This milestone was completed during the fourth quarter. Samples recovered from Li batteries at different stages of reaction were analyzed using short-range techniques such as XAS and TEM. The Ni $L_{II, III}$ edge spectra are shown in Fig. 1, left. They are consistent with the reduction of NiO to Ni during discharge (lithiation), and only partial re-oxidation during charge. Very similar results were obtained from electron diffraction data, in which spots for both NiO and Ni were observed at the end of charge (delithiation), confirming that the conversion reaction is not fully reversible. This irreversibility is likely behind the Coulombic inefficiency observed during the first cycle of a battery fabricated with materials that undergo conversion reactions. Electrode engineering may be required to achieve improvements in this direction.

The O K edge XANES data for the Ni material are shown in Fig. 1, right. While the spectrum after complete discharge (lithiation) is consistent with the presence of Li_2O, the signals observed at intermediate states and after delithiation up to 3 V (1 full cycle) cannot be explained by a combination of NiO and Li_2O, the only two components expected. The combination of data from two different detectors with different depth sensitivities confirmed that these spectra were representative of both the sample bulk and surface properties. Similar results were also found by EELS. These results suggest that other intermediate phases are formed during the charge and discharge processes.

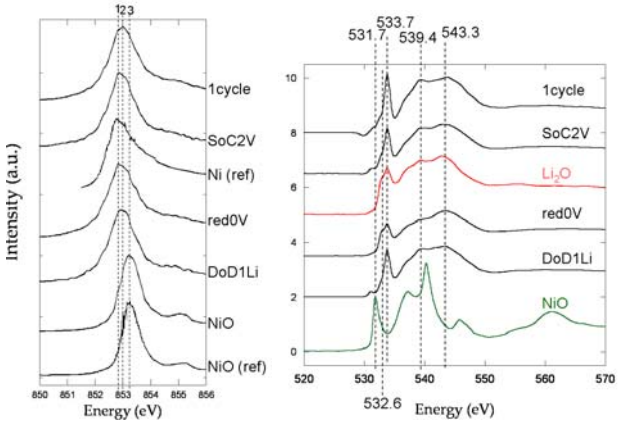


Figure 1. Ni $L_{II, III}$ (left) and O K (right) edge XANES data of NiO samples cycled in a Li battery. Reference spectra for NiO, Ni and Li2O are also included. 1: 852.8 eV, 2: 853 eV, 3: 853.2 eV.

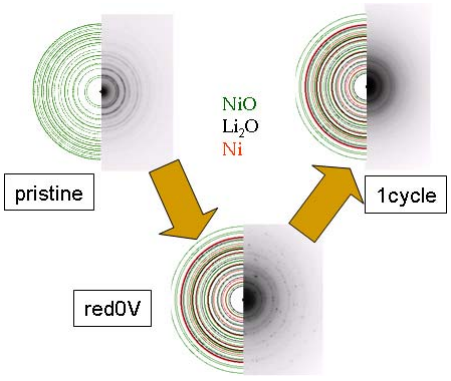


Figure 2. Electron diffractograms of NiO cycled in a Li battery.

Milestone B: This task will be phased out due to a change in project priorities and because no satisfactory results were obtained. No oxide-based phases containing Cu and another element were identified to have acceptable electrochemical performance.

TASK 7.4 - INVESTIGATOR, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Predicting and Understanding New Li-ion Materials Using *Ab Initio* Atomistic Computational Methods

SYSTEMS: High-voltage, high-energy: Gr/1 M $LiPF_6$ in EC:DEC (1:2)/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

BARRIERS: High cost, low energy, low rate, poor cyclability.

OBJECTIVES: 1) Predict new chemistries and crystal structures for improved electrodes as defined by the goals of USABC. 2) Understand rate-limiting behavior in current electrode materials in order to target and design optimal diffusion properties in new materials.

GENERAL APPROACH: Use computational *ab initio* atomistic modeling methods to predict new Li-ion battery electrode materials. Combine and provide efficient access to all relevant calculated knowledge in a searchable database, which will greatly facilitate computational materials design. Evaluate stability and potential synthesis issues of proposed compounds using calculated phase diagrams, phase competition, and oxygen chemical potential ranges. Use statistical mechanics models to understand Li diffusion limitations in existing electrode materials and design new materials with improved rate capabilities.

STATUS OCT. 1, 2009: The analyses of Li diffusion in bulk graphite have been concluded. Evaluation of Al-substitution effect on $LiNi_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO_2$ in terms of Li mobility and electronic conductivity has been studied. Phase diagrams of several Li-Cu-M-O (M= polyanion metal) compounds have been analyzed.

EXPECTED STATUS SEP. 30, 2010: A searchable database, which efficiently handles computations, analyses, and presentation of calculated materials properties, will be underway. Promising Li-Cu-M-O systems will be analyzed based on calculated electronic, Li diffusion, and stability properties. Understanding of rate-limiting phenomena in graphite and graphitic carbons (especially at low temperature) will be concluded.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; Operating charging temperature: -30 to 52ºC

MILESTONES:
(a) Evaluate rate-limiting phenomena in graphite. (Nov. 09) **Complete**
(b) Quantify the changes in Li mobility and electronic conductivity in $LiNi_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO_2$, as a function of Al content. (Mar. 10) **Complete**
(c) Evaluate electronic properties and phonon spectra of $LiCoO_2$, $LiMn_2O_4$ spinel, and $LiFePO_4$. (Sep. 10) **Delayed, due Dec. 10**
(d) Characterize and evaluate different Cu-Metal-O electrode compounds that can combine high voltage copper extrusion with a stable M-O framework to facilitate stability and good cyclability. (Sep. 10) **Delayed, due Nov. 10**

PROGRESS TOWARD MILESTONES

Collaborations: Gerbrand Ceder (MIT), Jordi Cabana (LBNL), Robert Kostecki (LBNL).

- In collaboration with Robert Kostecki and Jordi Cabana, water and water related specie surface absorption were investigated. In the atomistic modeling effort, studies were conducted to determine which graphitic surfaces are susceptible to water absorption and which are not. It was found that water (as expected) does not absorb on the inactive 0001 surface. However, the surface edges (shown in Fig.1) do absorb most species, although preliminary calculations indicate that more ionic species, such as hydrogen, oxygen and hydroxyl groups, absorb more strongly than water. This work showed that the edge sites on graphitic plans are highly active for absorption, which will significantly contribute to the contamination of both graphitic anodes as well as carbon black.

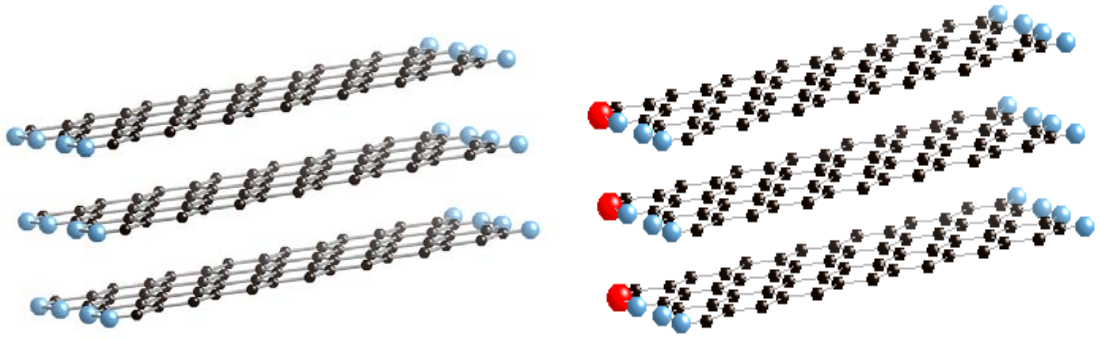


Figure 1. Picture showing the atomic arrangements for hydrogen and hydroxyl absorption on an edge graphite surface.

- Inspired by Dahn's work on anion intercalation into carbon and graphite, different anion specie insertions between graphitic planes were investigated. The qualitative trend with layer spacing of the different species was found to be consistent with experimental results. Furthermore, it was found that the orientation of the anion was crucial to minimize the strain within graphitic sheets. Figure 2 shows the buckling of the graphite planes as a result of an unfavorably oriented PF_6^- molecule.

- The calculation of phonon spectra of Li cathode materials has been postponed until December 2010 due to the delay in the hiring of a new postdoctoral associate.

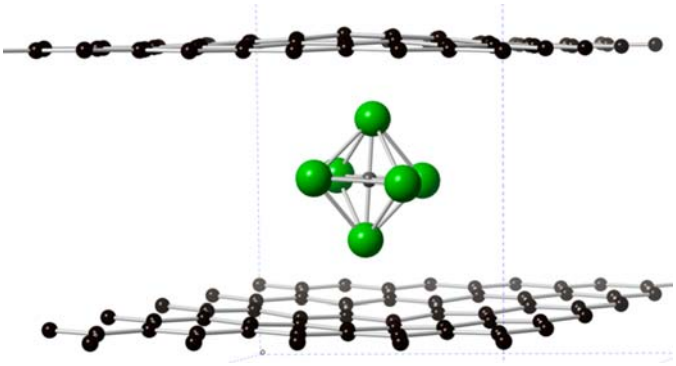


Figure 2. An intercalated PF_6^- molecule between graphitic sheets, which show significant strain due to the molecule's orientation.